

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1939.

Classification of chelating groups. H. M. HAENDLER and B. P. GEYER (J. Amer. Chem. Soc., 1938, 60, 2813—2814).—An abbreviated nomenclature for chelating groups is detailed. R. S. C.

Selenious anhydride as an oxidising agent in organic chemistry. N. N. MEL'NIKOV (Uspechi Chim., 1936, 5, 443).—The use of SeO_2 to oxidise paraffins, olefines, and alcohols to glycolaldehydes, substituted acetylenes to OH-acetylenes, terpenes to terpene ketones, aldehydes and ketones to keto-aldehydes, cyclic ketones to 1:2-diketones, mercaptans to disulphides, sulphides and disulphides to sulfoxides and sulphones, and *G*-methylamides to amide-aldehydes, is recommended. Amines, alcohols, and mercaptans give Se derivatives at low temp.

CH. ABS. (c)

Nonanes. β -Methyloctane, γ -ethylheptane, $\beta\gamma$ -dimethylheptane, and $\beta\beta\delta\delta$ -tetramethylpentane. F. C. WHITMORE and (Miss) H. A. SOUTHWATE (J. Amer. Chem. Soc., 1938, 60, 2571—2573).— $\text{CH}_2\text{Bu}^\gamma\text{CMe}_2\text{Br}$, b.p. $75^\circ/36$ mm., or, better, $\text{CH}_2\text{Bu}^\gamma\text{CMe}_2\text{Cl}$, b.p. $53^\circ/29$ mm., with ZnCl_2 gives 18% of $\beta\beta\delta\delta$ -tetramethyl-*n*-pentane, b.p. 120 — $125^\circ/730$ mm., m.p. -66.9° to -67.1° . Dehydration of *n*- $\text{C}_6\text{H}_{13}\text{CMe}_2\text{OH}$, $\text{CET}_2\text{Bu}^\alpha\text{OH}$, and $\text{CMePr}^\beta\text{Bu}^\alpha\text{OH}$ by heating with I and hydrogenating (Ni on Al_2O_3) the resulting olefines gives β -methyl-*n*-octane, b.p. 142.8° , m.p. -80.1° , γ -ethyl-*n*-, a glass, b.p. 143.1° , and $\beta\gamma$ -dimethyl-*n*-heptane, b.p. 140.65° , respectively. *n*, *d*, and η are also determined.

R. S. C.

Synthesis of tertiary hydrocarbons. F. C. WHITMORE and H. P. OREM (J. Amer. Chem. Soc., 1938, 60, 2573—2574).— β -Methyl-*n*-hexane, b.p. 90.3° , m.p. -120.3° , β -methyl-*n*-octane, γ -ethyl-*n*-heptane, γ -methyl-*n*-nonane, b.p. 167.6° , m.p. -90° , and δ -methyl-*n*-decane, b.p. 188.1° , m.p. -92.9° , are obtained in 23.7—48.8% yield from $\text{CMe}_2\text{Bu}^\alpha\text{OH}$, *n*- $\text{C}_6\text{H}_{13}\text{CMe}_2\text{OH}$, $\text{CET}_2\text{Bu}^\alpha\text{OH}$, *n*- $\text{C}_6\text{H}_{13}\text{CMeEtOH}$, and *n*- $\text{C}_6\text{H}_{13}\text{CMePr}^\alpha\text{OH}$, respectively, by passing in HI, then adding Zn, and passing in HCl at 70 — 80° . Prep. of the alcohols is also described, and *n* and *d* are determined.

R. S. C.

Hexamethylethane and tetra-alkylmethanes. R. E. MARKER and T. S. OAKWOOD (J. Amer. Chem. Soc., 1938, 60, 2598).—Addition of CuI to $\text{CR}_3\text{R}'$ and $\text{MgR}'\text{Hal}$ in Et_2O gives 11—20% of $\text{CR}_3\text{R}'$ ($\text{R} \neq \text{H}$). $\text{Bu}^\gamma\text{Cl}$ thus gives CMe_3Et , $\text{CMe}_3\text{Pr}^\alpha$, $\text{CMe}_3\text{Bu}^\alpha$, and *n*- $\text{C}_5\text{H}_{11}\text{CMe}_3$. CMe_2EtCl gives CMe_2Et_2 , $\text{CMe}_2\text{EtPr}^\alpha$, $\text{CMe}_2\text{EtBu}^\alpha$, and *n*- $\text{C}_5\text{H}_{11}\text{CMe}_2\text{Et}$. $\text{Bu}^\gamma\text{MgI}$ and $\text{Bu}^\gamma\text{Cl}$ similarly give 16% of C_2Me_6 , m.p. $>99^\circ$.

R. S. C.

Peroxide effect in the addition of reagents to unsaturated compounds. XVIII. Addition of and substitution by bisulphite. M. S. KHARASCH, E. M. MAY, and F. R. MAYO (J. Org. Chem., 1938, 3, 175—192; cf. A., 1938, II, 345).—In presence of O_2 NaHSO_3 adds to olefines, CR_2CH_2 , giving the "abnormal" product, $\text{CHR}_2\text{CH}_2\text{SO}_3\text{Na}$. NO_3' or NO_2' also causes addition. Thus, C_3H_6 , *iso*- C_4H_8 , $\text{CH}_2\text{CHCH}_2\text{OH}$, and $\text{CHPhCHCO}_2\text{H}$ give $\text{Pr}^\alpha\text{SO}_3\text{Na}$, $\text{Bu}^\delta\text{SO}_3\text{Na}$, $\text{OHCHEtSO}_3\text{Na}$ (I), and $\text{CO}_2\text{HCH}_2\text{CHPhSO}_3\text{Na}$, respectively. CHPhCH_2 gives similarly a little $\text{CHPhMeSO}_3\text{Na}$ (II), but mainly $\text{CHPhCHSO}_3\text{Na}$ (III). (III) arises by substitution, since $\text{CH}_2\text{PhCH}_2\text{SO}_3\text{Na}$ is unaffected by NaHSO_3O_2 . (I) is obtained also from $(\text{CH}_2)_3\text{Br}_2$ and aq. Na_2SO_3 and is identified by conversion by PCl_5 in CCl_4 into a lachrymatory chloride and thence by $\text{NH}_3\text{Et}_2\text{O}$ into γ -chloropropane- α -sulphonamide, m.p. 63° . $\text{CH}_2\text{PhCH}_2\text{Br}$ gives β -phenylethane-sulphonic acid (NHPhNH_2 salt, m.p. 154°), also obtained from $\text{CH}_2\text{PhCH}_2\text{SH}$ (IV) (prepared from $\text{Ph}[\text{CH}_2]_2\text{SOCH}_2\text{CO}_2\text{H}$) and converted by PCl_5 into the chloride, m.p. 34° , and thence via the amide, m.p. 121° , into $\text{CH}_2\text{PhCH}_2\text{SO}_2\text{Na}$ (V) and $\text{CH}_2\text{PhCH}_2\text{HgCl}$, m.p. 165° . With $\text{C}_6\text{H}_5\text{Cl}(\text{NO}_2)_2$ (IV) gives 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{S}[\text{CH}_2]_2\text{Ph}$, m.p. 88° , and thence the corresponding sulphone, m.p. 131° , obtained also from (V). CHPhMeCl and $\text{Na}_2\text{SO}_3\text{NaOH}$ give α -phenylethane- α -sulphonic acid (VI) (NHPhNH_2 salt, m.p. 115°), reconverted by PCl_5 into CHPhMeCl . Oxidation of CHPhMeSH yields (VI), and $\text{C}_6\text{H}_5\text{Cl}(\text{NO}_2)_2$ gives 2:4-dinitrophenyl CHPhMe sulphide, m.p. 109° [corresponding sulphone, m.p. 161° (decomp.)]. $(\text{CHPhCHSO}_3)_2\text{Ba}$ and PCl_5 give the acid chloride, m.p. 87° , and thence the amide, m.p. 142° , and Zn β -phenylethylene- α -sulphonate. NHPhNH_2 β -phenylethylene- α -sulphonate, m.p. 148° , 2:4-dinitrophenyl styryl sulphide, m.p. 158° , and styrylmercurichloride, m.p. 207° , are described. These results correct those of Ashworth *et al.* (A., 1928, 994). Electronic reaction mechanisms for the addition and substitution are discussed. R. S. C.

Instability of liquid isobutene. E. E. ROPER (J. Amer. Chem. Soc., 1938, 60, 2699—1701).—A liquid, probably a polymeride of relatively high b.p., with f.p. -100° to -120° and n_D^{20} 1.397—1.435, has been isolated from isobutene which has been kept for some time. Evidence points to dimerisation as the first step. At 0° this reaction causes a 0.6% lowering of the v.p. of pure isobutene.

E. S. H.

Reactions in sulphuric acid. Destruction of acetylene.—See A., 1939, I, 33.

Effect of the triple linking on rate of reaction of ω -chlorides with potassium iodide in acetone.—See A., 1939, I, 31.

Influence of structure on the rate of racemisation of organic halogeno-compounds. H. BÖHME [with O. SIERING] (Ber., 1938, 71, [B], 2372—2381; cf. Bodendorf *et al.*, A., 1935, 454).—CHPhMeCl (1 mol.) is completely racemised by SnCl_4 (0.001 mol.) in C_6H_6 within a few hr.; the addition of 0.001 mol. of HCl greatly retards racemisation, which is further retarded but not completely inhibited by 0.01 mol. of HCl. The effect is ascribed to the equilibrated production of an additive compound of SnCl_4 and HCl. Racemisation is ascribed to the formation of a complex between SnCl_4 and CHPhMeCl whereby the distance between C and Cl is increased and the intramol. electrical contrast is increased. The complex therefore dissociates into its ions which are configuratively labile. The alternative possibility of an equilibrium, $\text{CHPhMeCl} \rightleftharpoons \text{CHPh}\cdot\text{CH}_2 + \text{HCl}$, is shown to be improbable. CHMeEtCl is not racemised by SnCl_4 (1:1) in C_6H_6 in one day. After several days CHMePrCl is unaffected by HgCl_2 in COMe_2 or by SnCl_4 in C_6H_6 . $\text{CH}_2\cdot\text{CH}\cdot\text{CHMeCl}$ is not racemised by SnCl_4 (1:0.001 mol.) in C_6H_6 after several hr. but with 0.01 mol. of SnCl_4 the change has a half-period of 126 min. The half-period of the action with HgCl_2 (1:1) is about 77 hr. The effect is more pronounced with CHMe $\cdot\text{CH}\cdot\text{CHMeCl}$. $\text{CH}_2\text{Ph}\cdot\text{CHMeCl}$ is not racemised by SnCl_4 . α -cyclohexylethyl chloride is unchanged by SnCl_4 (1:0.05) but with SnCl_4 (1:0.12) the half-period of racemisation is 3 hr. CHMeCl $\cdot\text{CO}_2\text{Et}$, $\text{CO}_2\text{H}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CO}_2\text{Et}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ appear unchanged by SnCl_4 (1:1) after two days. CHPhCl $\cdot\text{CO}_2\text{Et}$ is not racemised by SnCl_4 (1:1). Crotyl chloride, b.p. $-2^\circ/18$ mm., from crotyl alcohol, $\text{C}_5\text{H}_5\text{N}$, and PCl_5 at 0° , and dimethylvinylmethyl chloride, b.p. $-5^\circ/26$ mm., appear new. (—)-Methylvinylmethyl chloride has b.p. $-5^\circ/26$ mm., $\alpha = -2.52^\circ$ ($l = 0.5$). H. W.

Complex between nitrobenzene and carbon tetrachloride.—See A., 1939, I, 26.

Primary active amyl halides. F. C. WHITMORE and J. H. OLEWINE (J. Amer. Chem. Soc., 1938, 60, 2570—2571).— d -CHMeEt $\cdot\text{CH}_2\cdot\text{OH}$ (I) with SOCl_2 - $\text{C}_5\text{H}_5\text{N}$ or PBr_3 gives 77% of d -CHMeEt $\cdot\text{CH}_2\text{Cl}$, b.p. $50.5\text{--}51^\circ/140$ mm., $[\alpha]_D^{25} +1.66^\circ$, and 29% of d -CHMeEt $\cdot\text{CH}_2\text{Br}$, b.p. $69.6^\circ/140$ mm., $[\alpha]_D^{25} +3.75^\circ$, respectively, reconverted by the Grignard reaction (O_2) into (I) with only 10% of racemisation during the complete cycle. Action of MgI_2 on the d -benzoate, b.p. $140.2^\circ/20$ mm., gives 17.5% of a largely racemised iodide, b.p. $47.1^\circ/20$ mm., $[\alpha]_D^{25} +4.84^\circ$, from which an active alcohol could not be regenerated. R. S. C.

Active atom in heptachloropropane. C. BRÜCKNER (Österr. Chem.-Ztg., 1938, 41, 363; cf. A., 1938, II, 254).—Reaction of $n\text{-C}_3\text{H}_7\text{Cl}$ with MgMeI can give only $\text{CCl}_3\cdot\text{CCl}\cdot\text{CHCl}$ (I) + C_2H_6 or $\text{CCl}_3\cdot\text{CCl}\cdot\text{CCl}_2$ + CH_4 . (I) and CH_4 cannot be produced in the same direction. J. W. S.

Action of Grignard reagent on heptachloropropane. M. REBEK and G. MANDRINO (Österr. Chem.-Ztg., 1938, 41, 363—364; cf. A., 1938, II,

254 and preceding abstract).—Addition of MgMeI (3 mols.) to $n\text{-C}_3\text{H}_7\text{Cl}$ (1 mol.), followed by treatment with H_2O , yields a complex mixture of products, including $\text{C}_3\text{H}_7\text{Cl}_5$, a liquid of higher b.p., about equal vols. of CH_4 and C_2H_6 , and traces of MeCl . It is concluded that the reaction takes two courses, probably those suggested by Brückner and by the authors, respectively. Action of MgEtI on $n\text{-C}_3\text{H}_7\text{Cl}$ yields C_4H_{10} as the principal gaseous product, whilst $\text{C}_2\text{H}_5\text{Cl}_5$ reacts with MgMeI (1 mol.) yielding $\text{C}_2\text{H}_5\text{Cl}_3$ and C_2H_6 . J. W. S.

Nitromethane. Potential hazards in use. D. S. MCKITTRICK, R. J. IRVINE, and I. BERGSTENSON (Ind. Eng. Chem. [Anal.], 1938, 10, 630—631).— MeNO_2 , alone or with $\text{OMe}\cdot[\text{CH}_2]_2\cdot\text{OH}$, is liable to explode when subjected to high pressure or temp. F. N. W.

Reaction of esters with aluminium isopropoxide. R. H. BAKER (J. Amer. Chem. Soc., 1938, 60, 2673—2675).— Al n -, b.p. $280\text{--}284^\circ/12$ mm., and *sec.*-butoxide, b.p. $165\text{--}166^\circ/3$ mm., allyloxide (impure), m.p. $145\text{--}150^\circ$, *n*-hexadecoxide, m.p. 44° , and ethyleneglycoxide are obtained by heating $\text{Al}(\text{OPr}^i)_3$ with Bu^nOAc , *sec.*- BuOAc , $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OAc}$, $n\text{-C}_{16}\text{H}_{33}\text{OAc}$, and $(\text{CH}_2\cdot\text{OAc})_2$, respectively, and allowing the Pr^iOAc to distil. Bu^nOAc gives Al isopropoxide di-*tert.*-butoxide, m.p. $165\text{--}167^\circ$, sublimes at $160^\circ/14$ mm. $\text{OEt}\cdot\text{CH}_2\cdot\text{OAc}$ and $\text{Al}(\text{OPr}^i)_3$ give the products of decomp. of $\text{Al}(\text{OPr}^i)_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{OEt}$, namely, MeOAc , (?) HCO_2Pr^i , EtOAc , Pr^iOAc , and COMe_2 . R. S. C.

Synthesis of *cis*- Δ^7 -hexenol (natural hexenol). M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1938, 21, 1542—1547).— COMeEt and PCl_5 give CMeEtCl_2 (yield scarcely 50%) which when dissolved in vaseline and added to NaNH_2 in the same medium at 170° gives $\text{CEt}\cdot\text{CH}$. This is dried by distillation over MgClO_4 and then over KOH and treated successively with MgEtBr and $(\text{CH}_2)_2\text{O}$, giving $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{OH}$ and Δ^7 -hexenol, b.p. $65.5\text{--}66^\circ/12$ mm. This is hydrogenated (colloidal Pd) to *cis*- Δ^7 -hexenol, b.p. $59\text{--}61^\circ/12.5$ mm. (3:5-dinitrobenzoate, m.p. $44.5\text{--}46^\circ$). The 3:5-dinitrobenzoate obtained from natural hexenol prepared from its phenylacetate derived from Japanese peppermint oil has m.p. $48\text{--}48.5^\circ$ and does not depress the m.p. of the synthetic product. The two hexenols are very similar but not identical in odour. II. W.

Influence of branched chains on optical activity. Configuration of propyl*tert.*-butylcarbinol. Relation between rotatory power and chemical character. P. G. STEVENS, W. E. HIGBEE, and R. T. ARMSTRONG (J. Amer. Chem. Soc., 1938, 60, 2658—2660).—The factor controlling $[M]$ in carbinols is the chemical effect due to branching of the chain and is paralleled by the amount of rearrangement occurring on dehydration or conversion into the chloride. d -CHMeBu γ -OH (I), b.p. 120° , $[M]_D +7.8^\circ$ (benzoate, $[M]_D +93.4^\circ$, $+86.3^\circ$ in CHCl_3 ; phthalate, $[M]_D +159.7^\circ$ in CHCl_3), and *l*-CHPr α -Bu γ -OH are configurationally related to d -CHMeBu α -OH, but the $[M]$ of (I) is abnormally low, as (I) is the first member of its series. *d*-*n*-Propyl*tert.*-butylcarbinol [$\beta\beta$ -dimethyl-*n*-hexan- γ -ol], b.p. $74.5\text{--}75^\circ/36$ mm., $[M]_D +55.2^\circ$

(almost the max.) [acetate, b.p. 73—73.5°/20 mm., $[M]_D^{25} +59.3^\circ$ (max.); benzoate, b.p. 117.5—117.8°/4 mm., $[M]_D^{25} +19.9^\circ$ (max.), +20.7° (max.) in CHCl_3], is obtained from MgBu^+Cl and Pr^+CHO and by resolution of its *H* phthalate, $[M]_D^{25} -8.4^\circ$ in CHCl_3 , by strychnine. $\text{CHMe}^+\text{CH}^+\text{CHBu}^+\text{OH}$ has max. $[M]_D^{25} +23.5^\circ$ and gives a *H* phthalate, $[M]_D^{25} -16.2^\circ$ in CHCl_3 .
R. S. C.

Periodate oxidation of $\alpha\beta$ -glycols.—See A., 1939, I, 32.

α -Alkoxybutadienes. O. WICHTERLE (Coll. Czech. Chem. Comm., 1938, 10, 497—509).— β -Chlorobutaldehyde Me_2 acetal and KOH give a small amount of α -ethoxy- Δ^2 -butadiene, b.p. 37—38°/41 mm., which with acraldehyde (I) affords 2(5 ?)-ethoxy- Δ^3 -tetrahydrobenzaldehyde, b.p. 90°/10.7 mm., and with crotonaldehyde yields the 2(5 ?)-ethoxy-6-methyl compound, b.p. 93—96°/10.5 mm. β -Chlorobutaldehyde Pr^2 acetal and KOH form a mixture of α -propoxybutadiene (III), b.p. 35.5—36.5°/13 mm., crotonaldehyde Pr^2 acetal, b.p. 75—77°/13 mm., and $\alpha\gamma$ -tripropoxybutane, b.p. 116—118°/13 mm. (I) and (III) give 2(5 ?)-propoxy-, b.p. 103—104°/10.8 mm., and (II) and (III) form 2(5 ?)-propoxy-6-methyl- Δ^3 -tetrahydrobenzaldehyde, b.p. 112—115°/12 mm. The following are similarly obtained: α -n-butoxybutadiene, b.p. 53.5—54.5°/13.2 mm.; crotonaldehyde Bu^2 acetal, b.p. 103—104°/12 mm.; 2(5 ?)-n-butoxy-6-methyl- Δ^3 -tetrahydrobenzaldehyde, b.p. 127—129°/13 mm.; α -isobutoxybutadiene, b.p. 53—56°/13 mm.; crotonaldehyde Bu^2 acetal, b.p. 103.5—104.5°/12.3 mm.; and 6-methyl-2(5 ?)-isobutyl- Δ^3 -tetrahydrobenzaldehyde, b.p. 127—130°/13.5 mm. Mol. refractions of the compounds have been determined. F. R. S.

Preparation of the higher aliphatic glycol ethers from crotonaldehyde. R. KUHN and C. GRUNDMANN (Ber., 1938, 71, [B], 2274—2277; cf. A., 1937, II, 306).—In the presence of alcohols the condensation of crotonaldehyde (I) gives alkoxy-polyene aldehydes (II), as dark red to violet, cryst., very sparingly sol. ppts. which belong mainly to the C_{20} series but contain in addition to C_{16} compounds substances derived from 6 or 7 mols. of (I). The solvent is involved in the change. Thus MeOH yields a methoxypolyene aldehyde, hydrogenated to the glycol ether, $\text{OH} \cdot \text{C}_{20}\text{H}_{40} \cdot \text{OMe}$, m.p. 42—43°; oxidation with CrO_3 leads to methoxy-fatty acids. The colour and position of the absorption bands of (II) proves that the addition of alcohol has not caused any marked interruption in the conjugation of the double linkings. With piperidine acetate as catalyst the best yields are obtained in EtOH and Bu^+OH ; reaction proceeds less favourably in alcohols with an odd no. of C atoms and does not appear to occur in CS_2 or C_6H_6 . Comparatively few amines or their salts are efficient as catalysts, the most suitable being piperidine, piperazine, and morpholine, the performance of which depends greatly on the quality.
H. W.

Phosphoric oxide as catalyst of the polymerisation of olefines. I. Existence of "benzenedimetaphosphoric acids." F. JOSTES and J. CRONJÉ (Ber., 1938, 71, [B], 2335—2341).—The product obtained by the action of P_4O_{10} on C_6H_6 at

120° does not induce the union of C_6H_6 and Δ^2 -heptene to *n*-heptylbenzene and gives only a small proportion of dimeric heptene. When P_4O_{10} and C_6H_6 are heated at 110—120° according to Giran (A., 1898, i, 407; 1900, i, 147) the product has nearly the same wt. as the original P_4O_{10} ; similar observations are made at 200°. Treatment of it (without removal of C_6H_6) with EtOH and neutralisation with BaO appears to give *Ba Et₂ pyrophosphate*; the presence of Giran's Ba benzenedimetaphosphate or Ba tetradimetaphosphate is excluded. Contrary to Giran, the action of NH_3 on the product from P_4O_{10} and C_6H_6 does not lead to NH_4 benzenemonodimetaphosphate but probably to a partial *anhydride* of iminopyrophosphoric acid, $\text{O} \cdot \text{P}(\text{OH})_2 \cdot \text{NH} \cdot \text{PO}_2$, which yields a non-hygroscopic Ba salt, probably, $\text{O} \cdot \text{P}(\text{OH})_2 \cdot \text{NH} \cdot \text{PO}_3\text{Ba}$. The colour produced during the action of P_4O_{10} on C_6H_6 is due to the presence of thiophen. It appears, therefore, that Giran's benzenedimetaphosphoric acids do not exist; this is true also in the cases of PhMe and xylene. Giran's hypotheses on the course of the condensation of olefines and aromatic compounds in presence of P_4O_{10} are therefore irrelevant.
H. W.

Reactions of trialkyl phosphates, alkyl acetates, and *tert*.-butyl hypochlorite in the Friedel-Crafts syntheses. N. BERMAN and A. LOWRY (J. Amer. Chem. Soc., 1938, 60, 2596—2597).—With AlCl_3 and C_6H_6 , Et_3PO_4 gives PhEt, Pr^2 phosphate (b.p. 122—125°/15—16 mm.) or Pr^2OAc gives PhPr, Bu_3PO_4 or *sec*.- BuOAc gives *sec*.-BuPh, Bu^+OCl gives PhBu⁺, and $\text{CHMeBu}^2\text{OAc}$ gives CHPhMeBu². Pr^2OAc and AlCl_3 at 15—50° react, but Pr^2Cl was not isolated.
R. S. C.

Vinyl halide polysulphones. Peracetic acid as a catalyst for the reaction between sulphur dioxide and olefines. C. S. MARVEL and F. J. GLAVIS (J. Amer. Chem. Soc., 1938, 60, 2622—2626).— AcO_2H (which may be present in paracetaldehyde) causes reaction of $\text{CH}_2\text{:CHCl}$ and SO_2 to give an amorphous polymeride, $(\text{C}_4\text{H}_6\text{Cl}_2\text{SO}_2)_x$, darkens at 135—140°, m.p. 250—275°, which with liquid NH_3 gives, not a cyclic product as usual, but a substance, $(\text{C}_4\text{H}_6\text{Cl}_2\text{N}_2\text{SO}_2)_x$, with NH_4Ph gives a product, $(\text{C}_{10}\text{H}_{12}\text{NClSO}_2)_x$, slowly loses SO_2 in boiling dioxan, and is decomposed by hot aq. NaOH, giving a small amount of an aldehyde, $(\text{C}_3\text{H}_5\text{O})_x$ [2 : 4-dinitrophenylhydrazones, m.p. 127—129°]. $\text{CH}_2\text{:CHBr}$ gives similar products. Ascaridole causes formation of a 1 : 1 : 2 co-polymeride, m.p. 200—225°, of $\text{CH}_2\text{:CHCl}$, Δ^2 - C_5H_{10} , and SO_2 , and a 2 : 1 : 2 co-polymeride, m.p. about 280—285° (decomp.), of $\text{CH}_2\text{:CHCl}$, CPh:CH , and SO_2 . Allyl chloride gives a product, $(\text{C}_3\text{H}_4\text{ClSO}_2)_x$, m.p. 185—215°, decomp. 225—275°, in presence of AcO_2H , but $\text{CH}_2\text{:CH} \cdot \text{CH}_2\text{Br}$, $\text{CHCl:CCl} \cdot \text{CHMeCl}$, and *n*- $\text{C}_5\text{H}_{11} \cdot \text{CH:CHBr}$ give no polymeride. Cryoscopy of SO_2 and $\text{CH}_2\text{:CHCl}$ reveals a compound containing 60% of SO_2 , but Δ^2 - C_5H_{10} , CHPh:CH_2 , and $\text{CH}_2\text{:CH} \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$ form no compound.
R. S. C.

Formation of large ring monosulphides from halogenated sulphides with extended carbon chains. G. M. BENNETT and H. GUDGEON (J.C.S., 1938, 1891—1897; cf. A., 1938, II, 200).—The poly-

merisation and ring-closure of ω -halogenoalkyl sulphides, obtained (SOCl_2) from the hydroxy-sulphides derived from glycol chlorohydrins and KSMc , is studied. For ring-closure (observed in C_{12} , C_{14} , and C_{16} compounds), the halogenosulphide was heated at high dilution in a polar solvent; hydroxylic solvents [Bu^nOH , $(\text{CH}_2\text{OH})_2$, PhOH] were discarded as yielding alkoxy- or phenoxy-compounds, and in AcOH reaction was very slow; COPhMe was the most satisfactory. *Me 7-hydroxy-*, b.p. $133-134^\circ/10$ mm., gives *Me 7-chloro-heptyl sulphide*, b.p. $160-162^\circ/3$ mm. (*mer.* (*vs mercurichloride*), m.p. $60-61^\circ$). *Me 8-hydroxy-*, m.p. 12° , b.p. $135-138^\circ/10$ mm., gives *Me 8-chloro-octyl sulphide*, b.p. $113-116^\circ/3$ mm. (*mer.*, m.p. 75°). *Me 9-hydroxy-*, m.p. 22° , b.p. $138-142^\circ/9$ mm., gives *Me 9-chloro-nonyl sulphide*, b.p. $118-124^\circ/2$ mm. (*mer.*, m.p. $60-62^\circ$). *Me 10-hydroxy-*, m.p. 25° , b.p. $170-172^\circ/13$ mm., gives *Me 10-chloro-decyl sulphide* (I), b.p. $128-131^\circ/1$ mm. (*mer.*, m.p. $75-78^\circ$). *Me 12-hydroxy-*, m.p. 49° , gives *Me 12-chloro-dodecyl sulphide*, m.p. $3-4^\circ$, b.p. $140^\circ/1$ mm. (*mer.*, m.p. $62-64^\circ$). *Me 14-hydroxy-* (II), m.p. 38° , gives *Me 14-chloro-tetradecyl sulphide* (III), m.p. $13-14^\circ$, b.p. $155^\circ/1$ mm. (*mer.*, m.p. 68°). *Me 16-hydroxy-*, m.p. $54-56^\circ$, gives *Me 16-chloro-hexadecyl sulphide* (IV), m.p. 22° (*mer.*, m.p. $72-76^\circ$). *Me 18-hydroxy-*, m.p. 62° , gives *Me 18-chloro-octadecyl sulphide* (V), m.p. 31° (*mer.*, m.p. $91-94^\circ$). With PBr_3 in C_6H_6 , (II) gives *Me 14-bromotetradecyl sulphide* (VI) (*mer.*, m.p. $69-70^\circ$). When heated in AcOH , (I) is little changed; in $\text{C}_2\text{H}_5\text{Cl}_4$ (VII), a compound, $\text{C}_6\text{H}_5\text{Cl}_3$ (1:3:5-trichlorobenzene trichloride ?), m.p. $104-106^\circ$, b.p. $90^\circ/10$ mm., derived from (VII), is formed. In $(\text{CH}_2\text{OH})_2$ (VIII), (I) gives *Me 10-(2-hydroxyethoxy)decyl sulphide* (*mer.*, m.p. about 60°). In (VII) or (VIII), (II) gives no pure product. With KI in Bu^nOH , or NaI in boiling PhOH , (II) gives *Me 14-butoxy-*, m.p. $60-68^\circ$, and *14-phenoxy-tetradecyl sulphide*, m.p. $46-59^\circ$. When boiled in AcOH for 1 day, (VI) gives a small amount of a sulphonium salt, but after 1 week gives polymeric tetradecamethylene sulphide, and, after addition of HgCl_2 , the mercurichloride, m.p. 167° , of tetradecamethylene sulphide (IX) (cf. *loc. cit.*). When heated for 24 days in AcOH , (III) gives small quantities of a sulphonium chloride, a substance, m.p. $115-118^\circ$, and (IX). The last is obtained most readily from (III) and NaI in boiling COPhMe . MeI formed is removed in vac.; unless this is done, highly polymerised substances are formed during subsequent distillation. Treated similarly, (IV) gives polymeric hexadecamethylene sulphide, and, after addition of HgCl_2 , the mercurichloride, m.p. $164-166^\circ$, of hexadecamethylene sulphide, m.p. 61° (extinction angle, of one of three forms, 5°). Similarly (V) gives a polymeric sulphide, m.p. $60-77^\circ$ (mixed di- and tri-polymerides ?), and the mercurichloride, m.p. $121-125^\circ$, of octadecamethylene sulphide, m.p. 74° , b.p. $186^\circ/16$ mm. Chlorosulphides with 7, 8, 9, 10, and 12 C atoms and NaI in COPhMe give no monomeric or H_2O -sol. products, but only di- to tri-polymerides. Higher polymerides are produced by heating without solvent. The cyclic sulphides described have a musk-like odour.

E. W. W.

Esters of chlorosulphonic acid. W. W. BINKLEY with E. P. DEERING (J. Amer. Chem. Soc., 1938,

60, 2310-2311).—The b.p., $49.1^\circ/29$ mm., $42.3^\circ/10$ mm., $52.2^\circ/10$ mm., and $66^\circ/10$ mm., d_4 and n for CSO_2R ($\text{R} = \text{Me}$, Et , Pr^i , and Bu^t , respectively) (improved prep.) are reported.

R. S. C.

Optical crystallographic studies with the polarising microscope. II. Identification of the *p*-bromoanilides of lower aliphatic acids. W. M. D. BEYANT and J. MITCHELL, jun. (J. Amer. Chem. Soc., 1938, 60, 2748-2751; cf. A., 1938, II, 344).—M.p. (quoted in parentheses) and optical crystallographic data are recorded for Bu^t (112.0°), Bu^i (155.6°), *n*-valeric (I) (167.1°), isovaleric (II) (126.7°), *dl*-2-methylbutyric (III) (122.3°), 2,2-dimethylpropionic (155.7°), Δ^1 -butenoic (IV) (116.0°), methoxyacetic (55.3°), and pyruvic (167.8°) *p*-bromoanilides. Metastable, cryst. modifications of (I), (II), (III), and (IV) have been obtained from the molten substances.

E. S. H.

Kolbe's synthesis in the electrolysis of butyric acid.—See A., 1939, I, 35.

Reversibility of the reaction between triglycerides and glycerol. H. H. YOUNG, jun., and H. C. BLACK (J. Amer. Chem. Soc., 1938, 60, 2603-2605).—With boiling glycerol and a trace of Na_3PO_4 , trilaurin (I) gives a little α -monolaurin (II); in absence of a catalyst reaction is slower and gives also $\alpha\alpha'$ -dilaurin (III); with Na_2CO_3 (III) is formed. When (I) is distilled at 0.5 mm. (190°), some glycerol and (II) are formed; steam at 2.2 mm. causes the same disproportionation. Only traces of soap are obtained. Similar reactions with palmitins, stearins, ethylene dipalmitate, and $\text{OH}[\text{CH}_2]_2$ palmitate are described.

R. S. C.

Catalytic action of selenium on unsaturated compounds. M. YOKOYAMA and M. KOTAKE (J. Chem. Soc. Japan, 1936, 57, 183-186; cf. A., 1935, 829).—Heating oleic acid (I) with 3% of Se at 300° for 3 hr. (also in CO_2 or H_2) caused 70% reduction. The behaviour of elaidic, ricinoleic, linoleic, and erucic acids (II) and the isomerisation of (I) and (II) (with Se at 180°) were also studied.

CH. ABS. (c)

Fatty acids. IV. Purification of linolenic acid by fractional crystallisation of the fatty acids of linseed and perilla oils. Properties of this acid prepared by crystallisation and by debromination. G. Y. SHINOWARA and J. B. BROWN (J. Amer. Chem. Soc., 1938, 60, 2734-2738; cf. A., 1938, II, 82).—Linolenic acid, obtained 84.5-99% pure by crystallisation of the fatty acids of linseed and perilla oils from COMe_2 and light petroleum at -23° , -45° , -60° , and -75° , differs slightly in its const. from α -linolenic acid regenerated from the hexabromide, and is probably a mixture although its m.p. (about -11.5°) is sharp. Determination of the acid by its Br_2 no. is discussed.

R. S. C.

Kinetic examination of cyclisation problems and the preparation of lactones. M. STOLLET and A. ROUVÉ (Parfum. mod., 1935, 29, 207-215; Chem. Zentr., 1937, i, 1121).—The lactonisation of γ -hydroxy-tetradecanecarboxylic acid in presence of PhSO_3H was studied in C_6H_6 , PhMe , Et_2O , Bu_2O , and $\text{C}_2\text{H}_5\text{Cl}_2$. (Monomeric) cyclisation in C_6H_6 is favoured by low concn. of OH -acid, small activation energy, and

increase in temp. (for the unimol. reaction). The quantity of catalyst has no direct influence.

A. H. C.

Aqueous hydrolysis of β -butyrolactone.—See A., 1939, I, 32.

Odour and constitution in the series of deca- and undeca-lactones. M. STOLL and P. BOLLE (Helv. Chim. Acta, 1938, 21, 1547—1553).—Contrary to the experience of Stoll and Rouvé (A., 1937, II, 240) with compounds containing large rings, the double linking does not produce a marked augmentation of the intensity of the odour in the present instances. The odour of the γ -decalactone is considerably modified by the *cis*-double linking and its intensity is somewhat increased by ramification of the chain. Lactones obtained by dehydration with H_2SO_4 which are consequently mixtures of structural and spatial isomerides have more penetrating and less refined odours. Hexylcyclohexanone is transformed by $K_2S_2O_8$, H_2SO_4 , and K_2SO_4 at 0—10° into δ -hydroxyundecolactone, b.p. 152—155°/10.5 mm. The Mg derivative from *cis*-hexenyl chloride and iodide in Et_2O transforms $CH_2Ac\cdot CH_2\cdot CH_2\cdot CO_2Et$ into γ -hydroxy- γ -methyl- Δ^5 -undecenolactone, b.p. 136.5—137°/8.5 mm., and converts Et β -formylpropionate into γ -hydroxy- Δ^5 -undecenolactone, b.p. 80—81°/0.08 mm. $CHNa(CO_2Et)_2$ and *cis*- Δ^8 -nonadienyl chloride afford Et_2 nonadienylmalonate, b.p. 100—101°/0.03 mm., hydrolysed and decarboxylated to Δ^7 -undecadienoic acid, b.p. 104—107°/0.12 mm., which is lactonised by boiling 80% H_2SO_4 to *cis*- γ -hydroxy- Δ^7 -undecenolactone, b.p. 95—98°/0.15 mm., the position of the double linking in which is established by the formation of $EtCHO$ on ozonolysis. $CHNa(CO_2Et)_2$ and *cis*- Δ^7 -hexenyl iodide yield Et_2 *cis*- Δ^7 -hexenylmalonate, b.p. 131—133°/8.5 mm., which with $CH_2\cdot CH\cdot CH_2Br$ affords Et_2 allyl-*cis*- Δ^7 -hexenylmalonate, b.p. 144—146°/9 mm., hydrolysed and decarboxylated to α -allyl- Δ^8 -octenoic acid, b.p. 95—96°/0.05 mm.; this is transformed by Fittig's method into γ -hydroxy- α - Δ^7 -*cis*-hexenylvalerolactone, b.p. 80°/0.18 mm.

H. W.

Introduction of substituted vinyl groups. I. isoPropenylalkylmalonic esters. A. C. COPE and (Miss) E. M. HANCOCK (J. Amer. Chem. Soc., 1938, 60, 2644—2647).— $CM_2\cdot C(CO_2Et)_2$ (prep. described), best with $NaNH_2$ in liquid NH_3 , gives $CH_2\cdot CMe\cdot CNa(CO_2Et)_2$, which with the alkyl halide or sulphate gives Et_2 methyl-, b.p. 110—111°/12 mm., ethyl-, b.p. 117—119°/13 mm., allyl-, b.p. 122—123°/10 mm., propyl-, b.p. 132—133°/17 mm., isopropyl-, b.p. 114—116°/10 mm., butyl-, b.p. 137—138°/13 mm., isobutyl-, b.p. 131—132°/12 mm., *n*-amyl-, b.p. 147—148.5°/12 mm., and isoamyl-, b.p. 140—141°/11 mm., iso-propenylmalonate. Yields are good for introduction of primary, but moderate for that of *sec.*, alkyl. *n* and *d* are given. With Na in Et_2O much reduction occurs.

R. S. C.

Oxidation of θ -dihydroxystearic acids by periodic acid. η -Aldehydo-octioic acid. G. KING (J.C.S., 1938, 1826—1828).— θ -Dihydroxystearic acid (form of m.p. 132°) in $EtOH$ is oxidised by KIO_4 in $N\cdot H_2SO_4$ to nonaldehyde (I) and η -aldehydo-octioic acid (azelaic semialdehyde) (II) [*p*-nitrophenylhydr-

B* (A., II.)

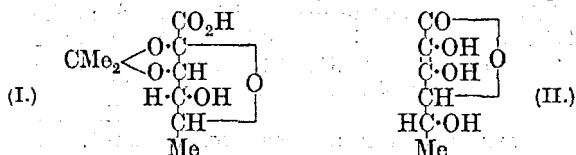
azone, new m.p. 144°; 2 : 4-dinitrophenylhydrazone, new m.p. 122.5° (cf. A., 1937, II, 48); semicarbazone, new m.p. 166.5°, with a small amount of a trimeride (III), m.p. 113.5°, of (II). θ -Dihydroxystearic acid (form of m.p. 95°) is oxidised similarly. Acid $KMnO_4$ oxidises (II) to azelaic acid, which is also formed, with (III), when (I) is kept. With $2N\cdot NaOH$ at 100°, (II) gives an oil, $(C_9H_{16}O_3)_4$. At higher concn. of HIO_4 and at 50—55°, (I) gives its trimeride.

E. W. W.

Esters of methanetricarboxylic acid. H. J. BACKER and J. LOKEMA (Rec. trav. chim., 1938, 57, 1234—1248).—The following diesters of $CH_2(CO_2H)_2$ (I) are prepared: *sec*.-Bu, b.p. 118°/12 mm.; Bu^v, m.p. -14°, b.p. 101.5—102°/15 mm., from Bu^vOH- $CH_2(COCl)_2$ -PhNMe₂ (cf. Gallus and Macbeth, A., 1938, II, 41); CH_2Et_2 , b.p. 136—137°/11—12 mm.; *n*-decyl, m.p. 17.5—18°, b.p. 216—217°/2.5 mm., from *n*-decyl alcohol, H_2SO_4 , and $CN\cdot CH_2\cdot CO_2K$ at 150° for 3 hr.; benzyl, b.p. 187°/1.5—2 mm., from (I), $CH_2Ph\cdot OH$, and H_2SO_4 at 120° for 2 hr.; *p*-nitrophenyl, m.p. 202—203° (decomp.), from $CH_2(COCl)_2$ and *p*-OH- $C_6H_4\cdot NO_2$ (water-bath), or from HNO_3 and $CH_2(CO_2Ph)_2$ at 0° for 10 min.; *p*-tolyl, m.p. 69°. The following triesters of methanetricarboxylic acid are prepared from the corresponding alkyl-malonate and -chloroformate in PhMe, e.g., $CHNa(CO_2Me)_2\cdot ClCO_2Me$ (boil for 4 hr.) afford $CH(CO_2Me)_3$, m.p. 46—47°, b.p. 132°/12 mm. (cf. Scholl and Egerer, A., 1913, i, 588) [*C*-Ac derivative, b.p. 149—150°/11—12 mm.; *C*-Bz derivative, m.p. 83°, b.p. 182—183°/2.5 mm. (cryst. form examined)]; *Pr*^a (prepared in Et_2O - C_6H_6), b.p. 160—161°/10 mm. (*Na* derivative); *Pr*^b, b.p. 139—140°/9—10 mm. [*Na* derivative and BzCl at 120° for 3 hr. give the Bz derivative, m.p. 88° (cryst. form examined)]; Bu^a, b.p. 147°/1—2 mm., 181—183°/11 mm. (*Na* derivative, m.p. 184°); Bu^b (II), b.p. 143°/2 mm., 171°/10 mm.; *sec*.-Bu, b.p. 139°/2.5 mm.; *n*-amyl, b.p. 173—174°/2 mm. (prepared at 130°), together with some amyl methane-tetracarboxylate; isoamyl (III), b.p. 175—176°/2.5—3 mm.; CH_2Et_2 , b.p. 145—146°/2 mm.; *n*-decyl (prepared in xylene), m.p. 14.5—15°, b.p. 208—210°/0.0015 mm.; cyclohexyl (in xylene at 100° for 7 hr.), b.p. 163—164°/0.0004 mm.; the *Me Pr*^b ester, b.p. 106.5—107°/2 mm., is prepared from $CH_2(CO_2Pr^b)_2$ and $ClCO_2Me$ (4 hr. at 100°). (II) and (III) with $NaOMe\cdot Et_2O$ do not give Na derivatives, but afford $CH_2(CO_2Me)_2$ and isobutyl and isoamyl alcohols respectively; the *n*-amyl ester shows similar partial decomp., although it yields a Na derivative. The Ph_3 ester, m.p. 168° (HNO_3 at -5° affords the *p*-nitrophenyl ester, m.p. 199—200°), is prepared by the above method (at 80° for 3 hr.), but also from $CHNa(CO_2Ph)_2\cdot Mg\cdot CCl_4\cdot Et_2O$ [$OEt\cdot Mg\cdot CH(CO_2Ph)_2$] and $EtOH\cdot ClCO_2Ph$ and decomp. the $MgCl\cdot C(CO_2Ph)_3$ with dil. H_2SO_4 ; some $CO(OPh)_2$ and $OPh\cdot CO\cdot OEt$ are formed also (cf. Lund, A., 1934, 869). The latter method is adopted to prepare the *tri-p*-tolyl, m.p. 109—110.5°; Ph_2 mono-*p*-tolyl, m.p. 110° [from $CH_2(CO_2Ph)_2\cdot ClCO_2\cdot C_6H_4Me\cdot p$], and Ph di-*p*-tolyl, m.p. 109—110° [from $CH_2(CO_2\cdot C_6H_4Me\cdot p)_2\cdot ClCO_2Ph$], methane-tricarboxylate. $OEt\cdot Mg\cdot CH(CO_2Ph)_2$ and BzCl- Et_2O afford benzoyldiphenylmalonate, m.p. 126.5—127.5°.

A. T. P.

6-Deoxy-*d*-araboascorbic acid [*d*-erythro-3-keto-6-methylpentonolactone]. W. T. J. MORGAN and T. REICHSTEIN (Helv. Chem. Acta, 1938, 21, 1459—1463). 2 : 3-*iso*Propylidene-*d*-fructomethyllose (A., 1938, II, 432) is cautiously oxidised by KMnO_4 to



$\alpha\beta$ -isopropylidene-*d*-glucomethyllosonic acid (I), m.p. 147—148° (corr.), $[\alpha]_D^{25} +10.7^\circ \pm 0.5^\circ$ in H_2O (*K* salt; *Me* ester, m.p. 95—96°). This is converted by EtOH —conc. HCl at 100° into COMe_2 and 6-deoxy-*d*-araboascorbic acid (II) (*Pb* salt), which is 100—150 times less active than ascorbic acid towards guinea-pigs.

H. W.

Dismutation of the carbonyl oxygen atom of aldehydes and ketones. N. BORGHELLO (Atti R. Ist. Veneto Sci. Lett., 1936, 95, II, 321—327; Chem. Zentr., 1937, i, 1404).—The view that carbonyl compounds contain, relative to O, a bivalent C united by secondary valencies or co-ordinatively to H and one or two univalent radicals is examined in the light of decomp. experiments. The decomp. of COMe_2 and EtCHO over catalysts into CO (180°) and its further conversion into CO_2 and C (>200°) proceeds equally easily so that the secondary linkings are of the same nature in both (cf. spectroscopic evidence, Henri, A., 1935, 10).

A. H. C.

Preparation and use of copper-chromium oxide catalysts for dehydrogenations. R. E. DUNBAR (J. Org. Chem., 1938, 3, 242—245).—Prep. of $\text{Cu-Cr}_2\text{O}_3$ on an inorg. support (best "celite," a clay) (a convenient form) and a simple apparatus for its use for the prep. of aldehydes from alcohols are described. 56.7 g. of $\text{Pr}^\text{C}\text{CHO}$ are obtained from 100 g. of $\text{Bu}^\text{C}\text{OH}$.

R. S. C.

Photo-decomposition of aldehydes and ketones.—See A., 1939, I, 35.

Dynamic isomerism of acetaldehyde-2 : 4-dinitrophenylhydrazones. W. M. D. BRYANT (J. Amer. Chem. Soc., 1938, 60, 2814—2815).—The forms, m.p. 168.5—170° and 156—157°, of $\text{CHMe:N-NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot 2 : 4$ (A., 1937, II, 5) are now considered to be dynamic isomerides. When cooled, the melt often gives a (?) equilibrium mixture, m.p. 148°.

R. S. C.

β -Chlorobutyric acetals. O. WICHTERLE and I. VAVRECKA (Coll. Czech. Chem. Comm., 1938, 10, 493—496).— MeOH , HCl , and crotonaldehyde give β -chlorobutaldehyde Me_2 acetal, b.p. 55—57°/19 mm.; the Pr^C , b.p. 102—104°/13 mm., Bu^C , b.p. 130—131°/17 mm., and Bu^C compounds, b.p. 129—130.5°/16 mm., are similarly prepared.

F. R. S.

Oxidation of semiacetals. L. SCHULZ (Schimmel & Co. Ann. Rept., 1938, 119—123).—Mol. proportions of $n\text{-C}_9\text{H}_{19}\text{CHO}$ and BzOH yield with CrO_3 , $n\text{-C}_9\text{H}_{19}\text{CO}_2\text{Bz}$ in 20% yield via the semiacetal; BzOBz is absent since PhCHO forms no semiacetal. $n\text{-C}_{12}\text{H}_{25}\text{OH}$ and $n\text{-C}_9\text{H}_{19}\text{CHO}$ give both dodecyl

decoate and decyl dodecoate in 50% yield since the semiacetals involved hydrolyse less readily. Semiacetals oxidise less readily than free alcohols and chloral-decylalcoholate gave (solid CrO_3 and C_9H_6) only 1.3% of decyl decoate with 17.7% of decyl trichloracetate. CrO_3 may be replaced by other H-acceptors (peroxides, peracids, etc.) capable of addition to the newly formed dipole of the semiacetals suggested as occurring thus: $\text{OH}\cdot\text{CHR}\cdot\text{O}\cdot\text{CH}_2\text{R}' + \text{X} \rightarrow \text{H}\cdots\text{X}\cdots\text{O}\cdot\text{CHR}\cdot\text{O}\cdot\text{CH}_2\text{R}' \rightarrow \text{O}\cdot\text{CR}\cdot\text{O}\cdot\text{CH}_2\text{R}' + \text{XH}_2$, but experiments to prove this mechanism in which $\text{X} = \text{R}'\text{CHO}$ were only partly successful since ester formation is accompanied by functional interchange.

T. F. W.

Enol acylates. H. SCHMIDT (Schimmel & Co. Ann. Rept., 1938, 124—126).—Boiling mol. proportions of the aldehyde and Ac_2O afforded *citral enol acetate*, a limpid oil with odour of geranyl acetate, *citronellal enol acetate*, a colourless oil with fresh odour, b.p. 110°/7mm., *isodecaldehyde enol acetate*, a colourless oil, pleasant odour, and *hydrocinnamaldehyde enol acetate*, a limpid oil, pleasant odour. The action of Ac_2O (2.5 mols.) and 100% H_3PO_4 (1 mol.) on the ketone (1 mol.) at -5° gave *pulegone enol acetate*, mint odour, having $\alpha_D +53^\circ 57'$, and *isopulegone enol acetate*, odour of menthyl acetate, $\alpha_D +22^\circ 16'$; both *l*-menthone, $\alpha_D -24^\circ$, and *d*-*iso*-menthone, $\alpha_D +84^\circ$, yield the same *menthone enol acetate* with an odour of menthyl acetate, $\alpha_D +64^\circ$. Piperitone and carvone yield phenol acetates with the enol acetates; no enol acetates were obtained from aliphatic or aromatic ketones and camphor. Enol acetates of saturated cyclic ketones give with Br and HBr, in most cases, bimol. products with loss of HBr, and catalytic hydrogenation is not possible. With Na and EtOH hydrolysis occurs, followed by reduction of the CO group.

T. F. W.

Interaction between methylene radicals and hydrogen. C. ROSENBLUM (J. Amer. Chem. Soc., 1938, 60, 2819—2820).—When irradiated by a "hot" Hg arc, keten gives CO and C_2H_4 . Mixtures of keten and H_2 , similarly irradiated at 35° and 200°, give 1 and 9.6%, respectively, of CH_4 and large amounts of saturated and polymerised hydrocarbons, indicating the reaction, $\text{CH}_2 + \text{H}_2 \rightarrow \text{Me} + \text{H}$.

R. S. C.

Bromination of aliphatic ketones. S. V. SHAH and D. G. PISHAWIKAR (Current Sci., 1938, 7, 182—183).—With an excess of liquid Br (4 days) COMe_2 gives a Br_8 , m.p. 72—73°, COMeEt and Ac_2 give Br_2 (m.p. 54° and 94°, respectively), COEt_2 , COPr_2 , COBu^C_2 , COBu^C_3 , and $\text{CO}(\text{C}_6\text{H}_{13})_2$ give Br_2 (b.p. 90—93°/4 mm., 120—123°/4 mm., 121—123°/4 mm., 129—132°/4 mm., and 162—165°/4 mm., respectively), $(\text{CH}_2\text{Ac})_2$ gives a Br_8 , m.p. 181°, and COMeBu^C gives a Br_2 -derivative, m.p. 69°. The reaction, initially slow, is catalysed by HBr produced. If x = no. of H on the C adjacent to CO and y = no. of CO in the compound, then $x - y$ = no. of Br introduced.

R. S. C.

Keto-ethers. III. β -Halogenoethoxyethyl alkyl ketone derived from ethylene bromohydrin. H. R. HENZE (J. Org. Chem., 1938, 3, 287).—Corrections (cf. A., 1938, II, 348).

R. S. C.

Steroids and sex hormones. XLVI. Syntheses with $\alpha\beta$ -diacetyethylene. M. W. GOLDBERG and P. MÜLLER (Helv. Chim. Acta, 1938, 21, 1699—1705).—CHAc:CHAc [improved prep. from (CH₂Ac)₂ and SeO₂ (cf. Armstrong and Robinson, A., 1934, 1337)] and CH₂:CMe:CMe:CH₂ in boiling C₆H₆ smoothly give 1:2-diacetyl-4:5-dimethyl- Δ^4 -cyclohexene, b.p. 135°/10 mm., m.p. 36—37° [disemicarbazone, m.p. 214.5° (corr.; decomp.)], slowly converted by boiling 0.1N-NaOMe into 3:5:6-trimethyl-4:7:8:9-tetrahydroindone, b.p. 145°/10 mm. [semicarbazone, m.p. 222—223° (corr.; decomp.)]. CNaMeAc-CO₂Et and COMe-CH₂Cl in Et₂O at 0° and subsequently at room temp. yield Et $\alpha\beta$ -diacetyl-isobutyrate (I), b.p. 120—121°/10 mm. Et $\alpha\beta$ -diacetyl-n-butyrate (II), b.p. 121—124°/10 mm., is derived similarly from CHNaAc-CO₂Et and COMe-CHBrMe. (III) when preserved and then warmed gives H₂O and Et 3-keto-2:5-dimethyl- Δ^4 -cyclopentenecarboxylate, b.p. 108°/15 mm., which is not sol. in alkalis and does not give a colour with FeCl₃. Hydrolysis of (II) is accompanied by extensive cyclisation whereas (III) is converted by boiling 20% aq. K₂CO₃ into $\alpha\beta$ -diacetylpropane, b.p. 73—74°/11 mm. This is transformed by aq. H₂SeO₃ into $\alpha\beta$ -diacetylpropene [γ -methyl- Δ^7 -propene- $\beta\epsilon$ -dione] (IV), b.p. 83—84°/10 mm., which does not give a colour with FeCl₃, and δ -hydroxy- γ -methyl- Δ^7 -propene- $\beta\epsilon$ -dione, b.p. 135°/15 mm., which rapidly becomes brown on contact with air, gives a violet-red colour with FeCl₃, and yields Ac₂ when ozonised. (IV) and CH₂:CMe:CMe:CH₂ afford 1:2-diacetyl-1:4:5-trimethyl- Δ^4 -cyclohexene, b.p. 141°/10 mm. H. W.

Quantitative formation of furfuraldehyde from xylose. E. E. HUGHES and S. F. ACREE (J. Res. Nat. Bur. Stand., 1938, 21, 327—336).—Examination of various methods of formation of furfuraldehyde (I) by distillation of xylose with 12% HCl shows that sources of error in determination of xylose by this method are decomp. and volatilisation of (I), effect of rubber stoppers, incompleteness of distillation, formation of (I) from hexuronic acid, and substances other than (I) and methylfurfuraldehyde in the distillate. A 100% yield of (I) is obtained by use of special apparatus with only glass in contact with hot vapours, and with a trap to prevent losses by evaporation from the distillate. 12% HCl saturated with NaCl is used and (I) removed by steam-distillation. J. D. R.

Behaviour of anhydromethylhexosides towards alkaline reagents. Preparation of derivatives of 3-aminoglucose and 2-aminoaltrose. S. PEAT and L. F. WIGGINS (J.C.S., 1938, 1810—1815).—Further examples are given of hydrolytic fission of a sugar anhydro-ring in two alternative directions. The glucose derivative formed rarely exceeds 10% of the product. 4:6-Benzylidene-2:3-anhydro- α -methylalloside (A., 1938, II, 349) with dry NH₃-MeOH at 150° gives, after 35 hr., a product, m.p. 162—166°, [α]_D²⁰ +119° (all rotations in CHCl₃ unless otherwise stated), and after 3 days a mixture acetylated to 4:6-benzylidene-3-acetamido- α -methylglucoside 2-acetate (I) (1 part), m.p. 270°, [α]_D²⁰ +44.6°, and -2-acetamido- α -methylaltroside 3-acetate (10 parts), m.p. 184°, [α]_D²⁰ +52.5°. With 0.5%

MeOH-HCl at 55°, followed by Ac₂O-NaOAc, (I) gives 3-acetamido- α -methylglucoside triacetate (II), m.p. 178°, [α]_D²⁰ +101.9°, of which the structure is established by prep. by other routes (see below). The mixed 3:4-anhydro- α -methylalloside and 3:6-anhydro- α -methylglucoside (III) [from the alkaline hydrolysis product of α -methylglucoside triacetate 3-*p*-toluenesulphonate (IV), from which the 2:3-anhydromethylalloside is removed as the CHPh derivative (cf. loc. cit.)] with MeOH-NH₃ at 150° give 3-amino- α -methylglucoside, m.p. 167—168°, [α]_D¹⁸ +144.4° in H₂O [acetylated to (II)], and (III); the gulose derivative, presumably also formed, was not isolated. The hydrolysis product of β -methylglucoside triacetate 3-*p*-toluenesulphonate, freed as before from the 2:3-anhydro- β -methylglucoside, and thus containing the 3:4-anhydro- β -methylalloside, gives with MeOH-NH₃ 3-amino- β -methylglucoside (hydrochloride, new m.p. 185°, new [α]_D²⁰ -35° in H₂O), which with Ac₂O-NaOAc yields 3-acetamido- β -methylglucoside triacetate, m.p. 160°, [α]_D¹⁸ -21.4°, converted by 2% MeOH-HCl into (II). With MeOH-NH₃ at 150°, (IV) gives (II), which with 6% HCl gives 3-aminoglucose (4-methylgulose not isolated), and with Me₂SO₄-NaOH-CCl₄ gives 3-acetamido-2:4:6-trimethyl- α -methylglucoside, m.p. 156° (decomp.), [α]_D¹⁷ +131.1°. With MeOH-NH₃ at 130°, dimethyl-3:4-anhydro- β -methylalloside (loc. cit.) gives 3-acetamido-2:6-dimethyl- β -methylglucoside 4-acetate, m.p. 142°, [α]_D²¹ -50.9°, which with Me₂SO₄-NaOH-CCl₄ forms 3-acetamido-2:4:6-trimethyl- β -methylglucoside, m.p. 134—135°, [α]_D²¹ -82.9°. Dimethyl-2:3-anhydro- β -methylalloside (V) with 5% MeOH-NaOMe gives 3:4:6-trimethyl- β -methylglucoside (5%) and 2:4:6-trimethyl- β -methylaltroside, a syrup (66%) (hydrolysed to 2:4:6-altrose, new [α]_D¹⁹ +38.2°). With 5% aq. KOH, (V) yields 4:6-dimethyl- β -methylaltroside, m.p. 118°, [α]_D¹⁹ -49.3°, further hydrolysed to 4:6-dimethylaltrose. 4:6-Benzylidene-2:3-anhydro- β -methylalloside and boiling 5% MeOH-NaOMe give 4:6-benzylidene-3-methyl- β -methylglucoside (VI) (12%), m.p. 166°, [α]_D¹⁷ -46.0°, and -2-methyl- β -methylaltroside (72%), m.p. 127—129°, [α]_D¹⁸ -48.0°. The glucosidic character of (VI) is shown by its giving, with Purdie's reagents, 4:6-benzylidene-2:3-dimethyl- β -methylglucoside. With aq. KOH, dimethyl-2:3-anhydro- β -methylalloside gives 4:6-dimethyl- β -methylaltroside, m.p. 118°, [α]_D¹⁹ -49.3° (from which a cryst. 4:6-dimethylaltrose was not obtained by acid hydrolysis), and 4:6-dimethyl- β -methylglucose.

E. W. W.

Syntheses with 5:6-anhydroisopropylidene-glucose. VII. Glucose 6-phenyl ether. H. OHLE, E. EULER, and R. VOULLIÈRE (Ber., 1938, 71, [B], 2250—2259).—5:6-Anhydroisopropylidene-glucose (I) and PhOH in presence of a trace of C₅H₅N at 110° give isopropylideneglucose 6-Ph ether (II) (+1H₂O), m.p. 61—62°, [α]_D²¹ -2.81° in CHCl₃, [α]_D²⁰ -11.17° in MeOH, -11.9° in 50% AcOH [diacetate (III), m.p. 109°, [α]_D²⁰ -10.16° in CHCl₃, -10.07° in AcOH; non-cryst. dibenzoate; 3:5-di-*p*-toluenesulphonate, m.p. 131°, [α]_D²⁰ +29.62° in CHCl₃]. (II) is converted by COMe₂-CuSO₄-H₂SO₄ into isodisopropylideneglucose 6-Ph ether, m.p. 133°, [α]_D²⁰ +31.40° in CHCl₃. 50% AcOH at 100° hydrolyses (II) to

α -glucose 6-*Ph* ether (III), m.p. 180° , $[\alpha]_D^{20} +140.5^\circ$ to $+88.32^\circ$ in C_5H_5N in 6 days, $[\alpha]_D^{20} +63.85^\circ$ in H_2O - C_6H_5N (1:1) (equilibrium after 2 min.); the *phenylhydrazone* is resinous whereas the *phenylosazone* has m.p. 174° , $[\alpha]_D^{19} -125.4^\circ$ to -73.4° . (III) and Ac_2O in C_5H_5N at -10° and then at 37° yield a mixture from which α -glucose 6-*Ph* ether 1:2:3:4-tetraacetate, m.p. 127° , $[\alpha]_D^{20} +117.4^\circ$ in $CHCl_3$, is isolated. The mixture is transformed by HBr - $AcOH$ at 20° into α -1-bromoglucose 6-*Ph* ether 2:3:4-triacetate, m.p. $93-94^\circ$, $[\alpha]_D^{20} +204^\circ$ in $CHCl_3$, converted by $AgOAc$ in $AcOH$ into β -glucose 6-*Ph* ether 1:2:3:4-tetraacetate, m.p. 142.5° , $[\alpha]_D^{20} +28.37^\circ$ in $CHCl_3$, and by Ag_2CO_3 in boiling $MeOH$ into β -methylglucoside 6-*Ph* ether 2:3:4-triacetate, m.p. $122-123.5^\circ$, $[\alpha]_D^{20} -2.66^\circ$ in $CHCl_3$; the latter compound is hydrolysed by NH_3 - $MeOH$ at 20° to β -methylglucoside 6-*Ph* ether, m.p. $135-136^\circ$, $[\alpha]_D^{20} -16.88^\circ$ in $COMe_2$, also obtained by direct glucosidification of (IV). (III) and boiling 50% $AcOH$ give a mixture of the α - and β -forms of glucose 6-*Ph* ether 3:5-diacetate. (I) and p - C_6H_4Br - OH give isopropylideneglucose 6-*p*-bromophenyl ether, m.p. 63° , $[\alpha]_D^{20} -4.64^\circ$ in $CHCl_3$, hydrolysed by boiling 50% $AcOH$ to α -glucose 6-*p*-bromophenyl ether, m.p. 166° , $[\alpha]_D^{20} +91.36^\circ$ to $+58.18^\circ$ in C_5H_5N in 92 hr. [*phenylosazone*, m.p. $200-201^\circ$ (decomp.); $[\alpha]_D^{20} -101.94^\circ$ to -55.80° in C_5H_5N]. The mixture of stereoisomeric glucose 6-*p*-bromophenyl ether tetra-acetates, m.p. $119.5-122^\circ$, becoming transparent at 127° , is converted by HBr - $AcOH$ into α -1-bromoglucose 6-*p*-bromophenyl ether 2:3:4-triacetate, m.p. $140-141^\circ$, $[\alpha]_D^{20} +169.7^\circ$ in $CHCl_3$, whence (Ag_2CO_3 in boiling $MeOH$) β -methylglucoside 6-*p*-bromophenyl ether 2:3:4-triacetate, m.p. 142.5° , $[\alpha]_D^{20} +3.02^\circ$ in $CHCl_3$. p - OH - C_6H_4 - OBz at 160° gives isopropylideneglucose 6-*p*-benzoyloxyphenyl ether, m.p. 166° , $[\alpha]_D^{20} -2.50^\circ$ in $CHCl_3$ (3:5-diacetate, m.p. 166° , $[\alpha]_D^{20} -15.83^\circ$ in $CHCl_3$). o - NO_2 - C_6H_4 - OH at $>140^\circ$ without catalyst yields isopropylideneglucose 6-*o*-nitrophenyl ether, m.p. 105° , or (+0.5 H_2O) m.p. $98-99^\circ$, $[\alpha]_D^{20} +7.16^\circ$ in $CHCl_3$, but cryst. compounds could not be obtained from *m*- or *p*- NO_2 - C_6H_4 - OH . β - $C_{10}H_7$ - OH at 140° affords isopropylideneglucose 6- β -naphthyl ether, m.p. $116-117^\circ$, $[\alpha]_D^{20} -80^\circ$ in $CHCl_3$ (3:5-diacetate, m.p. $131-132^\circ$, $[\alpha]_D^{20} -12.55^\circ$ in $CHCl_3$), whence α -glucose 6- β -naphthyl ether, m.p. $170-171^\circ$, $[\alpha]_D^{20} +98^\circ$ (const.) in C_5H_5N , $[\alpha]_D^{20} +88^\circ$ to $+59^\circ$ in C_5H_5N - H_2O (95:5) in 4 hr. [*phenylhydrazone*, m.p. 165° , $[\alpha]_D^{19} -8.75^\circ$ in C_5H_5N - $EtOH$ (4:6); *phenylosazone*, m.p. 187° , $[\alpha]_D^{19} -109.7^\circ$ to -103.9° in C_5H_5N - $EtOH$ (4:6) in 30 min.]. α -Glucose 6- β -naphthyl ether 1:2:3:4-tetraacetate, m.p. 162° , $[\alpha]_D^{20} +107.5^\circ$ in $CHCl_3$, is transformed by HBr - $AcOH$ at 20° into α -bromoglucose 6- β -naphthyl ether 2:3:4-triacetate, m.p. 141° , $[\alpha]_D^{20} +177.0^\circ$ in $CHCl_3$. This is converted by C_5H_5N and Ag_2SO_4 into the pyridinium sulphate, $C_{49}H_{52}O_{20}NS$, m.p. 151° , $[\alpha]_D^{20} +14.23^\circ$ in $CHCl_3$, by $AgOAc$ in $AcOH$ into β -glucose 6- β -naphthyl ether 1:2:3:4-tetraacetate, m.p. $165-166^\circ$, $[\alpha]_D^{20} +28.5^\circ$ in $CHCl_3$, and by Ag_2CO_3 and boiling $MeOH$ into β -methylglucoside 6- β -naphthyl ether 2:3:4-triacetate, m.p. 151° , $[\alpha]_D^{20} +6.0^\circ$ in $CHCl_3$. H. W.

Synthesis of 2:4:6-trimethylglucose and its relationship to yeast glucan. K. FREUDENBERG

and E. PLANKENHORN (Annalen, 1938, 536, 257-266).—3-Benzylideneisopropylideneglucose is converted into 3-benzylglucose and thence by Ac_2O and C_5H_5N at 30° into β -3-benzylglucose 1:2:4:6-tetraacetate (I), m.p., 107° , $[\alpha]_D^{20} -1.23^\circ$ in $CHCl_3$. This is hydrogenated (Pd - C in $AcOH$) to β -glucose 1:2:4:6-tetraacetate, m.p. 127° , $[\alpha]_D^{20} -13.5^\circ$ in $CHCl_3$ (whence β -glucose penta-acetate and 1:2:4:6-tetraacetate 3-*p*-toluenesulphonate, m.p. 174°), and converted in presence of Pt into β -3-hexahydrobenzylglucose 1:2:4:6-tetraacetate, m.p. 123° , $[\alpha]_D^{20} +1.1^\circ$ in $COMe_2$. Repeated methylation of (I) in $COMe_2$ by 50% KOH and Me_2SO_4 at room temp. and then at 50° gives 3-benzyl-2:4:6-trimethyl- $\alpha\beta$ -methylglucoside (II), b.p. $149^\circ/0.4$ mm., $[\alpha]_D^{20} +43.50^\circ$ in $EtOH$ (separation of α - and β -forms not attempted), from which by hydrolysis (5% HCl - $MeOH$ at 70°) 3-benzyl-2:4:6-trimethylglucose, m.p. $127-128^\circ$, $[\alpha]_D^{20} +54.6^\circ$ in $CHCl_3$, is obtained. With Na at 100° (II) gives 2:4:6-trimethyl- β -methylglucoside, m.p. $70-71^\circ$, $[\alpha]_D^{20} -19.3^\circ$ in H_2O (whence 2:4:6-trimethyl- β -methylglucoside 3-*p*-toluenesulphonate, m.p. 104° , $[\alpha]_D^{20} -47.45^\circ$ in $CHCl_3$), hydrolysed (5% HCl at 100°) to 2:4:6-trimethylglucose, m.p. 123° , $[\alpha]_D^{20} +108^\circ$ in $MeOH$, identical with the products of Haworth and Sedgwick (A., 1926, 1228) and Zechmeister and Tóth (A., 1934, 810). The following compounds are incidentally described: 3-benzylglucose 1:2:4:6-tetrabenzoate, m.p. 203° , $[\alpha]_D^{20} +8.6^\circ$ in $CHCl_3$; 3-nitrobenzylglucose 1-nitrate 2:4:6-triacetate, m.p. 116° , $[\alpha]_D^{20} +80.0^\circ$ in $CHCl_3$, from (I) and fuming HNO_3 in $CHCl_3$; 3-hexahydrobenzyl-1:2-acetonylglucose 5:6-diacetate, m.p. 66° , $[\alpha]_D^{20} -21.1^\circ$ in $CHCl_3$, by hydrogenation (Pt sponge in $AcOH$) of the corresponding 3- CH_2Ph compound; 3-benzyl-6-triphenylmethylglucose 1:2:4-triacetate (mixture of isomerides), m.p. 200° after softening at 145° , $[\alpha]_D^{20} +50.3^\circ$ in $CHCl_3$; dimethylanhydro- β -methylhexoside, b.p. $85^\circ/0.1$ mm., m.p. $47-48^\circ$, $[\alpha]_D^{20} -158.0^\circ$ in H_2O , by methylation of β -methylglucoside triacetate 3-*p*-toluenesulphonate (III) with $NaOH$ and Me_2SO_4 ; anhydro- β -methylhexoside diacetate, liquid, $[\alpha]_D^{20} -120^\circ$ in $CHCl_3$, by the successive treatment of (III) with $NaOEt$ in $CHCl_3$ and Ac_2O in C_5H_5N ; 3:6-anhydro- β -methylglucoside 2:4-diacetate, m.p. $78-79^\circ$, $[\alpha]_D^{20} -107^\circ$ in $CHCl_3$.

H. W.

Acetone [isopropylidene] derivatives of the sugars and their transformations. XXII. New conversion of isopropylideneglucose into 3:6-anhydroglucose. Stereochemistry of ethylene oxides. H. OHLE and H. WILCKE [with, in part, K. TESSMAR] (Ber., 1938, 71, [B], 2316-2327).—Addition to ethylene oxides occurs in three phases. The first consists of the union by the adding ions at the ends of the dipole of the mols., the second in the fission of a $C-O$ linking of the ethylene oxide ring to the zwitterion which in the third phase reacts with the adding ions. The first and third phases are, as ionic reactions, instantaneous and involve liberation of energy whereas the second requires energy and controls the rate of reaction. If the oxide contains no other polar group and the space fulfilment of the substituents permits an adequate approach of the adding ions to one of the two C atoms

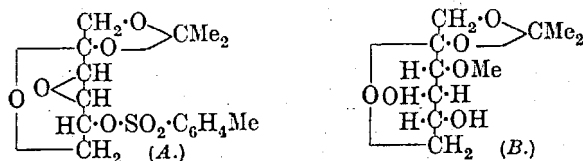
of the ethylene oxide ring in the direction of its dipole, addition is invariably accompanied by Walden inversion. If other polar groups are present their mutual influence changes the position of the dipole moment of the ethylene oxide group and the orientation of the adding ions is determined by the total moment of the mol. resulting from the combination of the individual moments. In these circumstances the addition of the anion can occur without Walden inversion and prediction of the course of addition is impossible.

*iso*Propyrideneglucose 5:6-diacetate 3-*p*-toluenesulphonate is hydrolysed by *N*-NaOH in boiling COMe_2 to *isopropylideneglucose* (I) in 83% yield; formation of an inner ether cannot be detected. Gradual addition of *N*-KOH to β -methylglucofuranoside 2:5:6-triacetate 3-*p*-toluenesulphonate in boiling aq. COMe_2 gives 3:6-anhydro- β -methylglucofuranoside, b.p. 141–142°/0.08 mm., m.p. 98°, $[\alpha]_D^{20} -49.5^\circ$ in H_2O (2:5-dibenzoate, m.p. 99°, $[\alpha]_D^{20} +2.8^\circ$ in CHCl_3 ; 2:5-di-*p*-toluenesulphonate, m.p. 130.5°, $[\alpha]_D^{20} +55.7^\circ$ in CHCl_3); it is hydrolysed by 0.03*N*- H_2SO_4 at 100° to 3:6-anhydroglucose, m.p. 110°, $[\alpha]_D^{20} +49.1^\circ$ in H_2O . *iso*Propyrideneglucose 5:6-dibenzoate 3-*p*-toluenesulphonate is transformed by $\text{HBr}-\text{AcOH}$ followed by addition of Et_2O into 1-bromo- β -glucofuranose 2-acetate 5:6-dibenzoate 3-*p*-toluenesulphonate, m.p. (indef.) 123–135°, $[\alpha]_D^{20} -101^\circ$ in CHCl_3 . Gradual addition of *N*-KOH to a boiling solution of β -methylglucofuranoside 2-acetate 5:6-dibenzoate 3-*p*-toluenesulphonate in aq. COMe_2 leads mainly to the non-cryst. 2:3-anhydro- β -methyl- α -allofuranoside 5:6-dibenzoate, $[\alpha]_D^{20} -96.2^\circ$ in EtOH , hydrolysed by boiling 2*N*-NaOH to 3:6-anhydro- β -methylglucofuranoside, m.p. 98°, $[\alpha]_D^{20} -49.6^\circ$ in H_2O . (I) and *p*- $\text{C}_6\text{H}_4\text{Me}-\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}-\text{CHCl}_3$ at 40° give *isopropylideneglucose* tri-*p*-toluenesulphonate, m.p. 129°, $[\alpha]_D^{20} -5.4^\circ$ in CHCl_3 . Titration of β -methylglucofuranoside 2-acetate 3:5:6-tri-*p*-toluenesulphonate in boiling COMe_2 with *N*-NaOH (phenolphthalein) affords 2:3-anhydro- β -methylallofuranoside 5:6-di-*p*-toluenesulphonate, m.p. 115.5–116°, $[\alpha]_D^{20} -26.3^\circ$ in CHCl_3 , in 78% yield. Under similar conditions β -methylglucofuranoside 2-acetate 6-benzoate 3:5-di-*p*-toluenesulphonate yields 2:3-anhydro- β -methylallofuranoside 6-benzoate 5-*p*-toluenesulphonate, m.p. 111°, $[\alpha]_D^{20} -45.0^\circ$ in CHCl_3 , in 66% yield. Hydrolysis of the pyroid β -methylglucoside 2:4:6-triacetate 3-*p*-toluenesulphonate (II) appears to give exclusively 3:4-anhydromethylalloside or a transformation product thereof. (II) is converted by TiCl_4 in CHCl_3 into α -methylglucopyranoside 2:4:6-triacetate 3-*p*-toluenesulphonate, m.p. 95–96° $[\alpha]_D^{20} +84.1^\circ$ in CHCl_3 .

H. W.

Acetone [*isopropylidene*] derivatives of the sugars and their transformations. XXI. Transformation of 1:2-*isopropylidene*- β -*D*-fructose into 3-methyl-*D*-sorbitose. Stereochemistry of the ethylene oxides. H. OHLE and C. A. SCHULTZ (Ber., 1938, 71, [B], 2302–2315; cf. A., 1935, 735). —1:2-*iso*Propylidene- β -*D*-fructose 3-benzoate (I), m.p. 197–199°, $[\alpha]_D^{20} -151.8^\circ$, is obtained in 90–95% yield by the action of 80% AcOH at 40° on 1:2:4:5-di-*isopropylidene*- β -*D*-fructose 3-benzoate, into which

it is re-converted by COMe_2 containing CuSO_4 . 1:2-*iso*Propylidene- β -*D*-fructose 3-acetate (II), m.p. 152–153°, is best prepared (yield 70%) from the 1:2:4:5-di-*isopropylidene* compound and 0.33*N*- H_2SO_4 in Pr^4OH at 40°. (I) and *p*- $\text{C}_6\text{H}_4\text{Me}-\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ at 40° slowly yield 1:2-*isopropylidene*- β -*D*-fructose 3-benzoate 4:5-di-*p*-toluenesulphonate (III), m.p. 164–165° (subsequent decomp.), $[\alpha]_D^{20} -175.0^\circ$ in CHCl_3 , from which a monotoluenesulphonate could not be prepared conveniently. 1:2-*iso*Propylidene- β -*D*-fructose 3-acetate 4:5-di-*p*-toluenesulphonate, prepared similarly, has m.p. 127–128°, $[\alpha]_D^{20} -119.5^\circ$ in CHCl_3 . 1:2-*iso*Propylidene- β -*D*-fructose 3-benzoate 4:5-di-2'-naphthalenesulphonate, decomp. about 150°, $[\alpha]_D^{20} -121.2^\circ$ in CHCl_3 , is described. (II) and 2- $\text{C}_{10}\text{H}_7-\text{SO}_2\text{Cl}$ (in suitable proportion) in $\text{C}_5\text{H}_5\text{N}$ at about 40° give 1:2-*isopropylidene*- β -*D*-fructose 3-acetate 4:5-di-2'-naphthalenesulphonate, m.p. 132–133°, $[\alpha]_D^{20} -100^\circ$ in CHCl_3 . Reduction of the relative amount of 2- $\text{C}_{10}\text{H}_7-\text{SO}_2\text{Cl}$ permits the isolation of (after subsequent acetylation) 1:2-*isopropylidene*- β -*D*-fructose 3:5-diacetate 4-2'-naphthalenesulphonate (IV), m.p. 142.5–143°, $[\alpha]_D^{20} -116.1^\circ$ in CHCl_3 , and 1:2-*isopropylidene*- β -*D*-fructose 5-acetate 3-benzoate 4-2'-naphthalenesulphonate, m.p. 135–136°, $[\alpha]_D^{20} -160.0^\circ$ in CHCl_3 . Attempts to remove the Bz group catalytically or with a mol. amount of NaOMe from (IV) were unsuccessful but it is converted by the gradual addition of *N*-NaOH to it in EtOH into 3:4-anhydro-1:2-*isopropylidene*- β -*D*-tagatose 5-*p*-toluenesulphonate (A), m.p. 117–118°, $[\alpha]_D^{20} -27.0^\circ$



in CHCl_3 . (IV) is converted by the successive action of NaOMe and $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ into 3:4-anhydro-1:2-*isopropylidene*- β -*D*-tagatose 5-acetate (V), m.p. 80–81°, $[\alpha]_D^{20} -28.6^\circ$ in CHCl_3 , whence 3:4-anhydro-1:2-*isopropylidene*- β -*D*-tagatose, m.p. 81–82°, $[\alpha]_D^{20} -80.7^\circ$ in CHCl_3 , $[\alpha]_D^{20} -60.0^\circ$ in H_2O , which is hydrolysed by 0.1*N*- H_2SO_4 to 3:4-anhydro- β -*D*-tagatose, m.p. 142–145° (subsequent decomp.), $[\alpha]_D^{20} -56.0^\circ$ to $+16.8^\circ$ in H_2O in 21 hr. (V) is transformed by Ac_2O , AcOH , and $\text{C}_5\text{H}_5\text{N}$ at 100° into 1:2-*isopropylidene*- β -*D*-fructose triacetate, m.p. 98.5–99.5°, $[\alpha]_D^{20} -135.7^\circ$ in EtOH , and converted by NaOMe in boiling MeOH into 3-methyl-1:2-*isopropylidene*- β -*D*-sorbitose (B), m.p. 121–122°, $[\alpha]_D^{20} -66.3^\circ$ in EtOH [with (?) 4-methylisopropylidene-fructose, b.p. 129–131°/0.08 mm., $[\alpha]_D^{20} -98.7^\circ$ in EtOH], which is transformed with difficulty into the Me_3 ether, b.p. 99–101°/0.2 mm.; $[\alpha]_D^{20} -59.6^\circ$ in H_2O . 3-Methyl-*D*-sorbitose has m.p. 152–153°, $[\alpha]_D^{20} -28.3^\circ$ in H_2O . 3:4-Anhydro-1:2-*isopropylidene*- β -*D*-tagatose 5-2'-naphthalenesulphonate, decomp. 140°, $[\alpha]_D^{20} -38.7^\circ$ in CHCl_3 , is described. The fission of the syrupy *isopropylidene*-fructose 3-acetate mononaphthalenesulphonate is discussed.

H. W.

Tritylation of α -*L*-sorbitose. Y. KHOUVINE and F. VALENTIN (Compt. rend., 1938, 207, 636–638).—

α -1-Methylsorboside with $\text{C}_6\text{H}_5\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$, followed by AcCl in $\text{C}_5\text{H}_5\text{N}$, affords 1-triphenylmethyl- α -1-methylsorboside 3:4:5-triacetate, m.p. (block) 185° , $[\alpha]_{\text{D}}^{25} +76.8^\circ$ in C_6H_6 , converted by AcOH-HBr into α -1-methylsorboside 3:4:5-triacetate, m.p. (block) 81° . 1:6-Ditriphenylmethyl-2:3-isopropylidene- α -1-sorbofuranose 4-acetate (cf. Ohle, A., 1938, II, 173) treated as above affords 2:3-isopropylidene- α -1-sorbofuranose 4-acetate, m.p. (block) 100° , $[\alpha]_{\text{D}}^{25} +23.0^\circ$ in CHCl_3 . 2:3:4:6-Diisopropylidene- α -1-sorbofuranose with $\text{C}_6\text{H}_5\text{Cl}$ affords 1-triphenylmethyl-2:3:4:6-diisopropylidene- α -1-sorbofuranose, m.p. (block) 182° , $[\alpha]_{\text{D}}^{25} -29.6^\circ$ in CHCl_3 . J. L. D.

Thermal decomposition of certain glucosides.

Z. JERZMANOWSKA and S. KŁOSÓWNA (Rocz. Chem., 1938, 18, 234—244).—Hyperin [from *Hypericum perf.*; identical with Sando's 3-galactosidylquercetin (A., 1937, II, 206)] and Ac_2O (2 hr. at the b.p.) yield hyperin octa-acetate, amorphous, m.p. $100-105^\circ$. This, when heated at $200^\circ/0.001$ mm., yields 2-hydroxy-d-galactal tetra-acetate and quercetin 5:7:3':4'-tetra-acetate (I), m.p. $159-160^\circ$. Quercetin hepta-acetate decomposes analogously, at $250^\circ/0.001$ mm., to yield (I) and 2-hydroxy-l-rhamnal triacetate, m.p. 74° , $[\alpha]_{\text{D}}^{25} +65^\circ$ in CHCl_3 . The thermal decomp. of phloridzin hepta-acetate proceeds differently, the products being β -glucose penta-acetate and 5-hydroxy-7-acetoxy-4-[β -(4'-acetoxyphenyl)ethyl]coumarin, m.p. $120-121^\circ$. Arbutin acetate distils unchanged at $200-250^\circ/10$ mm., whilst at higher pressures it undergoes profound decomp., to yield tarry products, of which only $p\text{-C}_6\text{H}_4(\text{OAc})_2$ was identified. R. T.

Heterosides of feebly basic amines.

M. FRÈRE-JACQUE (Compt. rend., 1938, 207, 638—640; cf. A., 1936, 716).—Glucose with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in AcOH-MeOH at 60° affords β -glucosidyl- p -nitroanilide, m.p. about 175° (Ac_4 , m.p. $\sim 155^\circ$, and Ac_3 , m.p. $\sim 161^\circ$, derivatives). The following are prepared similarly: β -mannosidyl-, m.p. $\sim 209^\circ$ (Ac_4 derivative, m.p. $\sim 184^\circ$), β -galactosidyl-, m.p. $\sim 203^\circ$ (Ac_4 and Ac_3 derivatives, m.p. indefinite and $\sim 140^\circ$, respectively), and β -rhamnosidyl-, m.p. $\sim 208^\circ$ (Ac_3 derivative, m.p. $\sim 209^\circ$), p -nitroanilide; β -glucosidyl-, m.p. $\sim 175^\circ$ (Ac_4 derivative, m.p. $\sim 136^\circ$), β -mannosidyl-, m.p. $\sim 199^\circ$, and β -rhamnosidyl-, m.p. $\sim 150^\circ$, m -nitroanilide; β -mannosidyl- o -nitroanilide, m.p. $\sim 196^\circ$ (Ac_4 derivative, m.p. $\sim 126^\circ$). Vals. for $[\alpha]_{\text{D}}^{25}$ are listed. Solutions of the above compounds in $\text{C}_5\text{H}_5\text{N}$ or H_2O are not mutarotatory. The heterosides with cold $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ afford Ac_3 or Ac_4 derivatives; in the presence of ZnCl_2 at 100° , Ac_5 derivatives are formed. J. L. D.

Hemicelluloses from cottonseed hulls. E. ANDERSON, J. HECHTMAN, and M. SEELEY (J. Biol. Chem., 1938, 126, 175—179; cf. A., 1932, 47).—By fractional pptn. and chlorination or bromination of the unknown impurity (I), white hemicelluloses are obtained from cottonseed hulls in two fractions, having 1 mol. of d -glucuronic acid (II) combined with 10 and 15 mols. of d -xylose. In the unhalogenated products, (I) and (II) bear a constant ratio.

Macromolecular compounds. CCII. Oxidative degradation of celluloses in phosphoric acid. H. STAUDINGER and I. JURISCH (Ber., 1938, 71, [B], 2283—2289).—The viscosity of solutions of cellulose (I) in H_3PO_4 is determined before and after addition of so much KMnO_4 as is necessary to cause fission of the mol. of (I) to half its degree of polymerisation. The amount of O required for this purpose does not depend greatly on the type of (I) and is somewhat greater for the more highly polymerised than for the somewhat degraded products. Marked chemical change is caused in 7.5 g. of (I) by 1 mg. of O. Since the amount of (I) is not appreciably altered by degradation it follows that O attacks the glucose residues within the chain and not at the ends. Possibly the thread mols. of (I) are not quite uniformly constructed and at certain points possess reactive groups which the oxidising agent attacks with particular readiness. H. W.

Structure of cellulose ethers obtained by the methylation of cellulose materials dispersed in quaternary ammonium bases. J. COMPTON (J. Amer. Chem. Soc., 1938, 60, 2823).—Dispersions of wood pulp or viscose rayon in $(\text{CH}_2\text{Ph})_2\text{NMe}_2\cdot\text{OH}$ with Me_2SO_4 gives a product (I) (OMe 12—16%), converted by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ and subsequent heating with MeOH at 125° in 30—35% yield into α - (mainly) and β -methylglucoside and a syrup, which with $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ gives methyltrimethylglucoside acetate, methyltrimethylglucoside diacetate, α -methyl-2-methylglucoside triacetate, and β -methylglucoside tetra-acetate. Acetolysis of (I) gives 5% of cellobiose octa-acetate. (I) is thus similar to the product obtained by $\text{Cu}(\text{OH})_2\text{-NaOH}$ etc. Cellulose is thus dispersed in $(\text{CH}_2\text{Ph})_2\text{NMe}_2\cdot\text{OH}$ as particles, confirming the fact that particles of about 1 μ . diameter are made visible by the slit ultra-microscope.

R. S. C.

Relative rate of ring-closure reactions.—See A., 1939, I, 32.

$\beta\beta\beta'$ -Trichlorotriethylamine. J. P. MASON and D. J. GASCH (J. Amer. Chem. Soc., 1938, 60, 2816—2817).— $\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_3$, b.p. $143-144^\circ/5$ mm., prepared in 92% yield, is rather unstable. R. S. C.

Time factor in the interaction of amino-acids with sugars. M. FRANKEL and A. KATCHALSKY (Biochem. J., 1938, 32, 1904—1907; cf. A., 1937, II, 402; Balson and Lawson, A., 1938, II, 120).—At 20° and varying initial p_{H} no decrease in p_{H} occurs in aq. mixtures of non-aldehydic sugars (sucrose, fructose) and glycine to which NaOH is added, and the potentiometric titration curve is not affected by the length of the intervals between the additions of NaOH . When aldehydic sugars (glucose, galactose) are used the p_{H} is decreased, the extent of the rapid and marked decrease increasing when the intervals between additions of NaOH are increased. The decrease is not due solely to the acidity of the sugars.

W. McC.

Synthesis of dl -glutamic acid. C. S. MARVEL and M. P. STODDARD (J. Org. Chem., 1938, 3, 198—203).— dl -Glutamic acid (I) is obtained in 70—75% yield from $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ (II), $\text{CH}_3\text{CH}\cdot\text{CO}_2\text{Me}$ (III), and NaOEt-EtOH , or in 57%

yield from (II), $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and slightly > 1 mol. of NaOEt in EtOH [by way of (III)]. $\text{CHNa}(\text{CO}_2\text{Et})_2$ and (III) give *Me* γ -dicarbethoxy-*n*-butyrate, b.p. 156—162°/18 mm.; converted by $\text{Br}\cdot\text{CCl}_4$ into the γ -Br-ester, b.p. 129—133°/2 mm., which with NH_3 -MeOH gives Br⁺ but very little NH_2 -acid, and with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$ gives compounds, hydrolysed mainly to glutaric acid. $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CBr}(\text{CO}_2\text{H})_2$ and aq. NH_3 give γ -carboxy- γ -butyrolactone.

R. S. C.

Rotatory power of citrulline. Synthesis of the optically active product. R. DUSCHINSKY (Compt. rend., 1938, 207, 735—737).—Citrulline from the press juice of the water-melon (A., 1930, 1224) has m.p. 219—220°, $[\alpha]_D^{20} + 3.7^\circ$ in H_2O . *l*(+)-Ornithine treated by Kurtz's method yields *l*(+)-citrulline, m.p. 220—221°, $[\alpha]_D^{20} + 3.4^\circ$ in H_2O . $[\alpha]_D^{20}$ varies with p_H , as in the case of all $\alpha\text{-NH}_2$ -acids (cf. *ibid.*, 460).

J. L. D.

Methionine. I. Interaction of methionine and other amino-acids with mercuric chloride. G. TOENNIES and J. J. KOLB (J. Biol. Chem., 1938, 126, 367—379).—The ppt. obtained by the interaction of methionine (I) and HgCl_2 is $[\text{SMe}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2]_2\text{Hg} + 4\text{HgCl}_2$. Complete pptn. is favoured by neutrality, absence of Cl^- , presence of EtOH , and removal with $\text{Hg}(\text{OAc})_2$ of Cl^- produced by the interaction. Basic NH_2 -acids yield ppts. with HgCl_2 , and acid NH_2 -acids with Hg^{++} [from $\text{Hg}(\text{OAc})_2$] and hence should be removed before pptn. of (I). Neutral NH_2 -acids yield sol. compounds with HgCl_2 with liberation of HCl , the effect of which is counteracted by using excess of HgCl_2 and adding $\text{Hg}(\text{OAc})_2$ and alkali. W. McC.

Differences in the reactivity of thiol and disulphido-groups in organic compounds. A. SCHÖBERL and F. KRUMBEY (Ber., 1938, 71, [B], 2361—2371).—The method used for the determination of cystine (I) and cysteine (II) by phosphotungstic acid (III) (A., 1938, II, 211) can be extended immediately to SS- (IV) but not to SH- (V) -glutathione. In acetate buffer at p_H 5.2 (IV) reacts smoothly with Na_2SO_3 : $\text{G}\cdot\text{S}\cdot\text{S}\cdot\text{G} + \text{Na}_2\text{SO}_3 = \text{G}\cdot\text{SNa} + \text{G}\cdot\text{S}\cdot\text{SO}_3\text{Na}$, and (V) thus produced can be oxidised by (III). Since the S-S groups of (I) and (IV) have the same reduction equiv. towards (III) the determination of the purity of preps. of (IV) is simply effected by comparative measurements. At p_H 5.2 (V) does not reduce (III) as strongly as (II) and under these conditions the two compounds have not the same reduction equiv. but at p_H 7.3 the reducing power of (V) is equal to that of (II) at p_H 5.2. *iso*Cysteine and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ completely reduce (III) at p_H 5 and have high extinction coeffs. at p_H 4. The max. p_H for (I) is ~ 5 . $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ and (V) exhibit full reducing power at p_H 6. When the max. of a thiol is reached it is little influenced by further increase in alkalinity. α -SH acids display reducing power at lower p_H than do the corresponding β -SH acids. The experiments are not independent of the particular buffer used. Thus a PO_4''' buffer with p_H about 5.9 gives much smaller colour intensities with (V) and $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ than does an acetate buffer of like p_H whereas with α -SH acids this influence is

not observed. The action of Na_2SO_3 on S-S compounds also depends greatly on p_H , the yield of SH-compound increasing very rapidly with increase of p_H from 3.5 to 5.0; differences are encountered in different systems. $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ cannot be determined by (III) at p_H 5.2 but this is readily done at greater p_H , suitably in presence of NaHCO_3 . $(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$ is not attacked by Na_2SO_3 at p_H 12 and its colorimetric determination by means of (III) shows the firmness of the S-S linking. Even at p_H 13 the completion of the reaction remains uncertain. At higher temp. the colour intensities attain the expected vals. but there is a danger of hydrolysis of the S-S linking. H. W.

Decomposition of cystine in aqueous solution. J. I. ROUTH (J. Biol. Chem., 1938, 126, 147—154; cf. Shinohara *et al.*, A., 1934, 761).—Cystine when boiled with H_2O in air or N_2 gives H_2S and S (ratio $\sim 2:1$ after long boiling) and cysteine. The concn. of cysteine (determined by Shinohara's method) rises to a max. and then falls. Traces of acidic products are formed, but no NH_3 . A. LI.

Behaviour of carbamide on heating. J. KRUSTINSONS (Z. Elektrochem., 1938, 44, 790—791).— NH_3 is absorbed rapidly by $\text{CO}(\text{NH}_2)_2$ at 104—139°; at higher temp. the absorbed NH_3 is freed.

E. S. H.

Condensation of esters of unsaturated acids with carbamide. IV. Z. JERZMANOWSKA and I. GAMOTA (Rocz. Chem., 1938, 18, 245—249).— $[\text{C}(\text{CO}_2\text{Et})_2]_2$ (I) and $\text{CS}(\text{NH}_2)_2$ are heated with NaOEt in EtOH (30 min. at the b.p.), to yield thiohydrylic acid (II), instead of the expected thio*spiro*hydantoin. (II) originates from condensation with $\text{CS}(\text{NH}_2)_2$ of $[\text{CH}(\text{CO}_2\text{Et})_2]_2$, formed by reduction of (I) with NaOEt . R. T.

Carbonyl cyanide. II. R. MALACHOWSKI and H. PISARSKA (Ber., 1938, 71, [B], 2239—2240; cf. A., 1937, II, 282).— $\text{CO}(\text{CH}\cdot\text{N}\cdot\text{OH})_2$ is transformed by $(\text{EtCO})_2\text{O}$ at 60—65° into its *dipropionate* (I), m.p. 84—85°, which passes at 100—110°/1 mm. into EtCO_2H and *propionoximinoacetoneitrile*, b.p. 115°/1 mm., m.p. 43—44°; at 160—180°/130—140 mm. this gives $\text{CO}(\text{CN})_2$ in 31.2% yield. (I) is therefore not preferable to the corresponding acetate for the prep. of $\text{CO}(\text{CN})_2$. An improved prep. of $\text{OAc}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}\cdot\text{CN}$ is described. H. W.

Formation of α -aminoisobutyronitrile.—See A., 1939, I, 32.

Synthesis of creatinephosphoric acid. K. ZEILE and H. MEYER (Z. physiol. Chem., 1938, 256, 131—140; cf. A., 1938, II, 157).—Methylallylaniline, from $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ and NHPhMe , with HCl and NaNO_2 yields the corresponding NO-compound which, hydrolysed with alkali, gives methylallylamine (I). (I) with the sulphate of isomethylthiocarbamide gives *methylallylguanidine* [sulphate (II) with $0.5\text{H}_2\text{SO}_4$, decomp. 245°; *picrate*; *diphenylphosphate*, m.p. 77°, from (II) and $(\text{OPh})_2\text{POCl}$]. (II) with $\text{Ba}(\text{MnO}_4)_2$ gives creatine in 14% yield. The Ca salt of creatinephosphoric acid (III) with dry HCl at 103° for 3 hr. yields creatinine, inorg. PO_4''' , and a substance similar to or identical with the phosphate of methyl-

hydantoic acid (Ca salt). Na creatininephosphate with 0.1*N*-NaOH at 100° for 10 min. gives an approx. 100% yield of (III). *iso*Creatinephosphoric acid is identical with natural (III). The results and electrochemical data confirm the view that (III) is $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{PO}(\text{OH})_2$. W. McC.

Optical rotation of a Grignard reagent. F. C. WHITMORE and B. R. HARRIMAN (J. Amer. Chem. Soc., 1938, 60, 2821—2822).— CHMeEtBr , $[\text{M}]_D^{25} -4.35^\circ$, in Bu^n_2O gives a Grignard reagent, which after removal of excess of bromine, has $[\text{M}]_D^{25} +5.36^\circ$. R. S. C.

Reducing action of primary Grignard reagents with trimethylacetyl chloride. F. C. WHITMORE, R. E. MEYER, G. W. PEDLOW, jun., and A. H. POPKIN (J. Amer. Chem. Soc., 1938, 60, 2788—2789).—Addition of Bu^nCOCl to an excess of MgRCl gives $\text{CH}_2\text{Bu}^n\text{OH}$ (if $\text{R} = \text{Et}$ 0, Pr^n 20, Pr^i 23, Bu^n 28, Bu^i 61, n -20, and *iso*-amyl 71%) and $\text{CHBu}^n\text{R}\cdot\text{OH}$ (if $\text{R} = \text{Et}$ 69, Pr^n 76, Pr^i 53, Bu^n 71, Bu^i 26, n -75, and *iso*-amyl 71%). If $\text{R} = \text{Et}$, 20% of $\text{CEt}_2\text{Bu}^n\text{OH}$, and, if $\text{R} = \text{isoamyl}$, 7% of olefine, are formed. R. S. C.

Action of primary Grignard reagents with *tert*-butylacetyl chloride. II. F. C. WHITMORE, J. S. WHITAKER, K. F. MATTIL, and A. H. POPKIN (J. Amer. Chem. Soc., 1938, 60, 2790—2792; cf. A., 1938, II, 476).—Addition of MgRBr ($\text{R} = \text{Et}$, Pr^n , Bu^n , and *n*-amyl) to a slight excess of $\text{CH}_2\text{Bu}^n\text{COCl}$ gives $\text{CH}_2\text{Bu}^n\text{COR}$ (51, 37, 34, and 29%, respectively) and $\text{CH}_2\text{Bu}^n\text{CHR}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Bu}^n$ (7, 20, 23, and 21%, respectively). R. S. C.

Complex cuprohydrocyanide of hexamethylenetetramine. P. MESNARD (Bull. Trav. Soc. Pharm. Bordeaux, 1936, 74, 157—161; Chem. Zentr., 1937, i, 1212).—The complete analysis of the complex $\text{CuCN}_5[(\text{CH}_2)_6\text{N}_4\cdot\text{HCN}]$ (cf. A., 1938, II, 341) is described. A. H. C.

Cuprohydrocyanide reagent as a precipitant for methylene-blue. P. MESNARD (Bull. Trav. Soc. Pharm. Bordeaux, 1936, 74, 161—164; Chem. Zentr., 1937, i, 1212).—The compound $2\text{CuCN}\cdot 13(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}\cdot\text{Cl}\cdot\text{HCN})\cdot 5\text{HCN}$ (yield 60—70%) (analysis described) forms a violet-blue ppt. which becomes cryst. on boiling and again amorphous on drying. Unlike the compounds of alkaloids, it is insol. in the reagent on boiling. A. H. C.

Electronegativities of highly branched aliphatic groups. F. C. WHITMORE and H. BERNSTEIN (J. Amer. Chem. Soc., 1938, 60, 2626—2628).—By reaction of HgRR' with HCl the following relative electronegativities are established: $\text{Ph} > \text{Me} > \text{Et} > \text{Pr}^n > \text{Bu}^n$, $n\text{-C}_6\text{H}_{13} > \text{CH}_2\text{Bu}^n\text{CH}_2$, $\text{Bu}^n[\text{CH}_2]_3 > \text{sec-Bu} > \text{CHMeBu}^n$; $\text{CH}_2\text{Ph} > \text{Bu}^n > \text{CH}_2\text{Bu}^n$, which is remarkable, since CH_2Ph is less electronegative than other alkyl groups. *tert*-Butyl, m.p. 122—123° (decomp.), β -methylisobutyl, m.p. 117—118°, γ -methylisobutyl, m.p. 133—133.5°, pinacolyl, m.p. 89—90°, $\delta\delta$ -dimethyl-*n*-amyl, m.p. 104—105°, and *n*-octyl, m.p. 115—115.5°, mercuric chloride are prepared. $\text{CH}_2\text{Bu}^n\text{CH}_2\text{Cl}$, b.p. 115°, is obtained from the alcohol by $\text{SOCl}_2\text{-C}_6\text{H}_5\text{N}$. R. S. C.

Improved preparation of lead triethyl and lead trimethyl. F. HEIN and A. KLEIN [with, in part, E. NEBE] (Ber., 1938, 71, [B], 2381—2384).—Restricted passage of HCl into a dil. solution of PbEt_4 in Et_2O yields: a ppt. (I), $\text{PbEt}_3\text{Cl}\cdot\text{HCl}\cdot 1.5\text{Et}_2\text{O}$, readily sol. in 2*N*-KOH; continued passage gives a product, approx. PbEt_3Cl , which is very unstable and sparingly or slowly sol. in EtOH . PbEt_3 is readily obtained by electrolysis of a solution of (I) in the necessary amount of 2*N*-KOH between Pb electrodes under N_2 or CO_2 in a glass vessel the bottom of which is drawn out to a narrow tube and provided with a tap. PbEt_3 collects at the bottom of the vessel and is obtained as a lemon-yellow liquid by filtration after desiccation over Na_2SO_4 . Zn electrodes are less serviceable. PbEt_3Br can replace PbEt_3Cl . Alternatively, the solution of PbEt_3Cl , prepared as above, is heated with fine Al wire at 100°. The change proceeds also at room temp. if Al activated by preheating with alkali hydroxide, Pb pretreated with dil. HNO_3 , or Zn pretreated with HCl is used. PbMe_3 is obtained similarly. H. W.

Formation of organometalloidal and similar compounds by micro-organisms. VI. Further studies on the fission of the disulphide linkage. S. BLACKBURN and F. CHALLENGER (J.C.S., 1938, 1872—1878).—Air aspirated through aq. bread cultures of *Penicillium brevicaulis*, Saccardo (Baarn strain A), containing $(\text{Bu}^n\text{S})_2$ and passed through aq. $\text{Hg}(\text{CN})_2$ and HgCl_2 gives small amounts of Hg di-*n*-butylthiol (also obtained, with chloromercury *n*-butylthiol, m.p. 177—177.5°, from Bu^nSH and HgCl_2) and *Me n*-butyl sulphide dimercurichloride, m.p. 115—116.5° (also prepared from MeBu^nS). With di-*n*-amyl disulphide, b.p. 140.5—142°/17 mm. (from $n\text{-C}_5\text{H}_{11}\text{Br}$, EtOH , and $\text{Na}_2\text{S}_2\text{O}_3$, followed by KOH), and the culture, *Me n*-amyl sulphide, b.p. 144.5—145.5°/? mm. [mercurichloride, $3\text{SMe}\cdot\text{C}_5\text{H}_{11}\cdot 7\text{HgCl}_2$ (?), m.p. 126—127°], and probably $n\text{-C}_5\text{H}_{11}\cdot\text{SH}$ are formed. With $(\text{MeS})_2$ (new prep., free from mono- and poly-sulphide, from MeI , MeOH , and $\text{Na}_2\text{S}_2\text{O}_3$, followed by KOH) and the culture, a product, m.p. 135—141°, decomp. 156°, consisting of chloromercury methylthiol mercurichloride, $\text{SMe}\cdot\text{HgCl}_2\cdot x\text{HgCl}_2$, and Me_2S sulphide mercurichloride, is formed. Without the culture, $(\text{EtS})_2$ and aq. HgCl_2 give $\text{SEt}\cdot\text{HgCl}_2\cdot\text{HgCl}_2$ (cf. A., 1937, II, 271), and a filtrate which after removal of Hg^{++} and neutralisation gives EtSO_2Na , converted into $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{Et}$. $(\text{MeS})_2$ similarly gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{Me}$. MeSH and aq. HgCl_2 give a product, m.p. 141°, decomp. 156°, and a product, $(\text{MeS}\cdot\text{HgCl}_2?)$, m.p. $< 260^\circ$. Me_2S_3 gives a mixture of the compounds, $\text{SMe}\cdot\text{HgCl}_2\cdot x\text{HgCl}_2$ and $\text{HgCl}_2\cdot 2\text{HgS}$, and $(\text{Bu}^n\text{S})_2$ the compound, $\text{SBu}^n\cdot\text{HgCl}_2$. ($n\text{-C}_5\text{H}_{11}\cdot\text{S}$)₂ gives chloromercury *n*-amylthiol, m.p. 180.5°, also obtained, with di-*n*-amylthiol, from $n\text{-C}_5\text{H}_{11}\cdot\text{SH}$ and HgCl_2 . E. W. W.

Stereoisomeric hexaethylcyclohexanes. H. KOCH and H. STEINBRINK (Brennstoff-Chem., 1938, 19, 407—408).—Fractions, b.p. 153.3—154°, 154—155°, and 155—156°/16 mm., of the previously described hexaethylcyclohexane (A., 1938, II, 354) have yielded 2.5, 6.9, and 7.9%, respectively, of a cryst. form (I), m.p. 104.7—105° (corr.). Comparison

of the sp. refractions of the fractions before and after separation of (I) indicates that the liquid part is the *cis*- and that (I) is, therefore, the *trans*-form.

A. B. M.

Diene synthesis. VIII. Simple method in the dicyclo-[1:2:3]-octane series. K. ALDER and E. WINDEMUTH (Ber., 1938, 71, [B], 2404—2409).—Addition of AcOH to a solution of 2:5-*endo*-methylenhexahydrobenzylamine hydrochloride (A., 1938, II, 488) and NaNO₂ through which steam is passing gives dicyclo-[1:2:3]-octan-2-ol, m.p. 183° (phenylurethane, m.p. 130°; *H phthalate*, m.p. 116—117°), oxidised (cold K₂Cr₂O₇ and dil. H₂SO₄) to dicyclo-[1:2:3]-octan-2-one, m.p. 129° (*semicarbazone*, m.p. 171°; *monoanisylidene* compound, m.p. 91—92°). This is oxidised by HNO₃ (d 1.4) to cyclopentane-1-carboxylic-3-acetic acid, m.p. 139°; its Pb salt when dry distilled in CO₂ gives norcamphor. Dicyclo-[1:2:3]-octane has m.p. 141° (sealed capillary).

H. W.

Use of liquid amalgams in the analysis of nitro-derivatives of benzene homologues. M. I. PERRIER (Bull. Sci. Univ. Kiev, 1937, 3, No. 3, 37—41).—Minor improvements in the technique of the method previously described (A., 1937, II, 268) are recommended.

R. T.

Reversible replacement of aromatic halogen atoms. G. M. BENNETT and I. H. VERNON (J.C.S., 1938, 1783—1786).—Conditions are given for interchange of Cl, Br, and I in halogeno-2:4-dinitrobenzenes. 1:2:4-C₆H₃Cl(NO₂)₂ (I) and NaI (5 mols.) in boiling (CH₂·OH)₂ for ½ hr. give 30% of 1:2:4-C₆H₃I(NO₂)₂ (II), reconverted into (I) by excess of anhyd. LiCl in (CH₂·OH)₂. (I) and (II) with NaBr·(CH₂·OH)₂ afford some 1:2:4-C₆H₃Br(NO₂)₂, which gives (I) with LiCl. (I) and AgF, or dinitrophenyl *p*-toluenesulphonate and a chloride in (CH₂·OH)₂, give only 2:4:1-(NO₂)₂C₆H₃·OH. 1:3:4:6-C₆H₂Cl₂(NO₂)₂ and NaI in boiling (CH₂·OH)₂ for 5 min. give some 1:3:4:6-C₆H₂I₂(NO₂)₂. 1:3:4:6-C₆H₂MeCl(NO₂)₂ and NaI·(CH₂·OH)₂ for 5—30 min. also show incomplete conversion, yielding 70% of 3-iodo-4:6-dinitrotoluene, m.p. 108° (also prepared from *m*-C₆H₄MeI and HNO₃-H₂SO₄). The reaction C₆H₃I(NO₂)₂ + Cl' ⇌ C₆H₃Cl(NO₂)₂ + I' [in (CH₂·OH)₂ at 175° (cf. A., 1932, 26)] is shown to be reversible and bimol. With mol. quantities, it proceeds from either side towards an equilibrium at 68 mols. % of C₆H₃Cl(NO₂)₂, but some subsidiary reaction occurs. Velocity measurements are recorded. With 1:2:4-C₆H₃Br(NO₂)₂ and Cl' in (CH₂·OH)₂ at 175° (190°, 195°), the equimol. mixture tends from either side to an equilibrium with 23 mols. % of Br-compound.

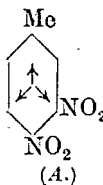
A. T. P.

Thermal decomposition of toluene; exclusive formation of benzyl radicals. F. HEIN and H. I. MESÉE (Naturwiss., 1938, 26, 710).—Decomp. of PhMe at 900—1100°/0.1—0.5 mm. yields only H and CH₂Ph· [identified by reaction with Hg vapour and subsequent conversion into CH₂Ph·HgBr (I)]. The absence of C₆H₄Me·HgBr in (I) is proved by quant. conversion into CH₂PhI and thence CH₂Ph·NEt₃I.

A. LI.

Aromatic nitro-derivatives. XV. 3:4-Dinitrotoluene: reactivity and nuclear configuration.

A. MANGINI and M. COLONNA (Gazzetta, 1938, 68, 543—554).—In 1:3:4-C₆H₃Me(NO₂)₂ (I), the 3-NO₂-group is the more reactive. On the Bonino formulation, the prevailing structure (A) is assigned to (I), in which, however, Me has a less powerful orienting influence than Cl or Br in 1:3:4-C₆H₃Hal(NO₂)₂, in agreement with the respective dipole moments. With NaOMe in boiling MeOH, (I) gives 4:1:3-NO₂·C₆H₃Me·OMe, with a phenolic substance, m.p. 120—127°, and an insol. product, m.p. 180—200°; the crude residue when reduced (Sn-HCl) and acetylated gives only 4:1:3-NHAc·C₆H₃Me·OMe. There is no evidence that any 3:1:4-NO₂·C₆H₃Me·OMe is formed. With NH₂Me·EtOH, however, (I) gives 4:1:3- (85%) and 3:1:4-NO₂·C₆H₃Me·NHMe (15%) (new prep. from 3:1:4-NO₂·C₆H₃Me·NH₂ and Me₂SO₄. With NHMe₂·EtOH, (I) gives 4-nitro-*NN*-dimethyl-*m*-toluidine (*picrate*, m.p. 125.5—126.5°), reduced (Sn-HCl) to 3-dimethylamino-*p*-toluidine (*picrate*, m.p. 136—137°; *Ac* derivative, m.p. 105—106°), which differs from 3:1:4-NH₂·C₆H₃Me·NMe₂. With NH₂Et·EtOH, 4:1:3-NO₂·C₆H₃Me·NHEt is formed. E. W. W.



Reactions of paraffins with aromatic hydrocarbons. I. Various paraffins with benzene. A. V. GROSSE, J. M. MAVITY, and V. N. IPATEV (J. Org. Chem., 1938, 3, 137—146).—Paraffins and C₆H₆ in presence of AlCl₃, when saturated with HCl and heated, usually at 135—175°, react mainly thus: RR' + HCl → RCl + R'H; RCl + ArH → ArR + HCl. The main intermediate RCl is EtCl, but many other fissions also occur. C₅H₁₂ (*n*- and *iso*-) gives PhEt + C₃H₈ and PhMe + C₄H₁₀. *n*-C₆H₁₄ and CHMe₂Pr^u give C₄H₁₀ + PhEt. *n*-C₇H₁₆ gives PhMe + C₆H₁₄, PhEt + C₅H₁₂, and PhPr + C₄H₁₀. *n*-C₈H₁₈ gives PhEt + C₆H₁₄ and PhPr + C₅H₁₂, but CHMeEtBu^u gives (readily at 80—90°, and even at 0°) only C₄H₁₀ + PhBu^u. *n*-C₁₀H₂₂ and *n*-C₁₆H₃₄ suffer fission at many places, giving C₄—C₁₁ hydrocarbons. The products are often isomerised during the reaction, e.g., *n*- to *iso*-C₄H₁₀, and PhR may give C₆H₆ + C₆H₄R₂, C₆H₃R₃, etc. Further, the reaction, RR' + 2C₆H₆ → RH + R'H + Ph₂, occurs, leading to extra yields of paraffin fission products. Slight decomp. of C₆H₆ itself to PhEt and other products occurs at 125—175°, but this decomp. is a main factor in the reaction with CH₄, C₂H₆, and C₃H₈, which occurs only at much higher temp.

R. S. C.

Derivatives of *s*-triethylbenzene. W. B. DILLINGHAM and E. E. REID (J. Amer. Chem. Soc., 1938, 60, 2606).—*s*-C₆H₃Et₃, b.p. 211.2°, is separated from the products of reaction of C₆H₆, C₂H₄, and AlCl₃ at 60—80° by virtue of its relative inertness to H₂SO₄ at 60—70° and liberation from its sulphonic acid at 110—125°. It is converted by standard methods into 2-nitro-1:3:5-triethylbenzene, b.p. 141.2°/7 mm., 2:4:6-triethyl-aniline, b.p. 135.5°/6 mm. (*Ac*, m.p. 149.5°, and *Bz* derivative, m.p. 181.3°), -phenol, b.p. 126.5°/mm. (*Me ether*, b.p. 100.8°/3 mm.), -benzonitrile, b.p. 108.5°/2 mm., and -benzeneazo-β-naphthol,

and 2 : 4 : 6 : 2' : 4' : 6'-hexaethyldiphenylthiocarbamide, m.p. 196.5°. R. S. C.

Polymerisation of styrene.—See A., 1939, I, 31.

Dimerisation of 3-phenylindene. C. S. MARVEL and H. A. PACEVITZ (J. Amer. Chem. Soc., 1938, 60, 2816).—3-Phenylindene with 47% HI or SnCl₄ gives a *dimeride*, m.p. 156—157°. The compound, m.p. 210—211°, of Blum-Bergmann (A., 1931, 208) could not be prepared. R. S. C.

Dimerisation of 3-phenylindene. E. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 2816).—The dimerides, m.p. 210—211° and 156—157°, of 3-phenylindene (cf. preceding abstract) are not allyl-isomeric forms, as they are not interconverted by NaOEt-EtOH. R. S. C.

Normal and destructive hydrogenation of naphthalene.—See B., 1938, 1389.

Reduction of nitronaphthalene with liquid zinc amalgam, for determination of nitro-groups. M. I. PERRIER and M. M. LOBUNETZ (Bull. Sci. Univ. Kiev, 1937, 3, No. 3, 43—48).—C₁₀H₇NO₂ is reduced by Zn-Hg in acid aq. EtOH or COMe₂, or in dil. HCl, and the resulting C₁₀H₇NH₂ is titrated with standard NaNO₂. The error is $\pm 3\%$. R. T.

Diene syntheses. IX. 1 : 4 : 5 : 8-Diendomethylenedecahydronaphthalene. K. ALDER and E. WINDEMUTH (Ber., 1938, 71, [B], 2409—2414).—2 : 5-endoMethylene- Δ^3 -tetrahydrobenzaldehyde and cyclopentadiene at 170—175° give 1 : 4 : 5 : 8-diendomethylene- Δ^6 -octahydronaphthalene-2-aldehyde, b.p. 142—143°/18 mm., hydrogenated (colloidal Pd in EtOH) to 1 : 4 : 5 : 8-diendomethylenedecahydronaphthalene-2-aldehyde (semicarbazone, m.p. 205°), the enol acetate, b.p. 155—165°/14 mm., of which is oxidised (KMnO₄-COMe₂-MgSO₄) to 2-keto-1 : 4 : 5 : 8-diendomethylenedecahydronaphthalene, b.p. 139—140°/11 mm. [semicarbazone (I), m.p. 206°]. The constitution of the ketone is established by its oxidation to *cis*-4 : 7-endomethylenehexahydrohydrindene-1 : 3-dicarboxylic acid (Alder *et al.*, A., 1932, 938). NaOEt-EtOH converts (I) at 190—200° into 1 : 4 : 5 : 8-diendomethylenedecahydronaphthalene, m.p. 36—37°, which appears sterically homogeneous. 1 : 4 : 5 : 8-Diendomethylene-2-decahydronaphthol, m.p. 93—95° and its *phenylurethane*, m.p. 117—119°, are described. H. W.

Action of benzaldehyde on *o*-, *m*-, and *p*-xylenes in presence of aluminium chloride. H. ELLISON and D. H. HEY (J.C.S., 1938, 1847—1853; cf. A., 1935, 344).—Dry CO passed into boiling C₆H₆-AlCl₃ for 6 hr. gives only a trace of CHPh₃, but CO + HCl (1 : 2) afford some anthracene (also obtained by using CO-AlBr₃). The yields are very small compared with those using PhCHO. The production of PhCHO is not an essential stage in forming the anthracene mol. (cf. Dewar and Jones, J.C.S., 1904, 85, 212; Egloff *et al.*, Chem. Rev., 1937, 20, 388). *o*-Xylene, PhCHO, and AlCl₃ at 60° for 6 hr. give 2 : 3 : 6 : 7-tetramethylantracene, m.p. 304° (corr.) (cf. Morgan *et al.*, A., 1931, 1282). *m*-Xylene, similarly, or with CH₂Cl₂-AlCl₃ at room temp., then at 60—80°, gives a mixture (A), m.p. 163—164° (const.

val. after several crystallisations), of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylantracenes, with (in first case) traces of a (?) *trimethylantracene*, m.p. 233—235°. Oxidation (CrO₃-AcOH) of (A) gives a mixture, m.p. 160—162°, of the corresponding anthraquinones; fractionation affords an impure quinone, m.p. $\sim 200^\circ$ (cf. Seer, A., 1912, i, 276; Friedel and Crafts, A., 1887, 1102). Similarly, *p*-xylene and PhCHO or CH₂Cl₂ give 1 : 4 : 5 : 8-tetramethylantracene, m.p. 270° (corr.) (-anthraquinone, m.p. 258—260°). Oxidation of a crude hydrocarbon from the mother-liquors (CH₂Cl₂ reaction) also gives a *tetramethylantracene*, m.p. 223—226°, probably resulting initially owing to migration of Me. Ph₂, PhCHO, and AlCl₃ in CS₂ at 35° for 5 hr., then 40° for 1 hr., or with CH₂Cl₂-AlCl₃ at 25° (4 hr.) and 45° (2 hr.), give a mixture, m.p. 312° (corr.), of 2 : 6- and 2 : 7-diphenylantracene, oxidised by CrO₃-AcOH to the corresponding mixed anthraquinones, m.p. 194—196°. The view (*loc. cit.*) that PhCHO supplies only the *meso*-C in the anthracene nucleus is substantiated; the linking uniting CHO to Ph is broken, and CO (active form) or HCOCi may be formed. A. T. P.

Dissociable anthracene oxides. Photo-oxides of 9-cyclohexyl- and 10-cyclohexyl-9-phenyl-anthracene. A. WILLEMART (Compt. rend., 1938, 207, 536—538; cf. A., 1938, II, 226).—Anthrone and 9-phenylanthrone with Mg cyclohexyl chloride afford 9-cyclohexyl- (I), m.p. 135—136°, and 10-cyclohexyl-9-phenyl-anthracene (II), m.p. 231—232°, respectively. The absorption spectra of these substances in CHCl₃ are analogous to those of 9-alkyl- and 9-phenyl-10-alkyl-anthracene. (I) and (II) with maleic anhydride form 1 : 1 adducts, m.p. $\sim 315^\circ$ and $\sim 340^\circ$, respectively. Insolation of (I) and (II) affords *photo-oxides*, C₂₀H₂₀O₂ and C₂₆H₂₄O₂, respectively; the former is stable when heated, whereas the latter gives 48% of O₂ (cf. A., 1936, 1101; 1937, 374). J. L. D.

Unsaturated steroids. IV. Preparation and photochemical oxidation of $\Delta^{2:4}$ -cholestadiene. E. L. SKAU and W. BERGMANN (J. Org. Chem., 1938, 3, 166—174; cf. A., 1937, II, 289).—A modified prep. and purification gives pure $\Delta^{2:4}$ -cholestadiene (I), m.p. 68.5°, $[\alpha]_D^{25} + 168.5^\circ$ in Et₂O (cf. *loc. cit.*), and a *cholestadiene* (II), m.p. 80—80.5°, $[\alpha]_D^{25} - 51.3^\circ$ in Et₂O, which has an absorption max. at 234 m μ ., and thus contains conjugated ethylenic linkings extending over two rings. Higher reaction temp. gives mainly (II). Pure (I) has absorption max. only at 267 and 275 m μ ., and is not carcinogenic. In EtOH-eosin and light with O₂ it gives the 2 : 5-peroxide (III), m.p. 113—114°, $[\alpha]_D^{25} + 48.3^\circ$ in CHCl₃ (cf. A., 1938, II, 227), which changes in m.p. and $[\alpha]$ when recrystallised; in EtOH-eosin and sunlight it gives [as does (I)] a (? non-peroxidic) *isomeride*, m.p. 166—168°, $[\alpha]_D^{25} + 141^\circ$ in CHCl₃ (cf. Butenandt *et al.*, A., 1938, II, 270). The structure of (III) follows from its hydrogenation (PtO₂) to a *diol*, C₂₇H₄₈O₂, m.p. 155°, $[\alpha]_D^{25} + 19.6^\circ$ in CHCl₃, which is unaffected by Pb(OAc)₄ and gives only a *monoacetate*, m.p. 141—142°, $[\alpha]_D^{25} - 9^\circ$ in Et₂O. R. S. C.

Symmetrical derivatives of chrysene. II. Elimination of methyl groups during dehydrogenation in attempt to prepare 1 : 10-dimethyl-

chrysene. W. E. JONES and G. R. RAMAGE (J.C.S., 1938, 1853—1858; cf. A., 1938, II, 228).—Et *meso*- β -diphenylbutane- $\alpha\delta\delta$ -tetracarboxylate, new m.p. 86°, heated with 85% H_2SO_4 for 3 hr. gives *trans*-2 : 11-diketo-1 : 2 : 9 : 10 : 11 : 18-hexahydrochrysene (cf. A., 1933, 828). Benzil, $\text{CHMeBr}\cdot\text{CO}_2\text{Me}$, and $\text{Zn}\cdot\text{C}_6\text{H}_6$ with a trace of MgMeI in Et_2O at 100° (bath)/3 hr. give β -benzoyl- α -methylcinnamic acid (I), m.p. 235°, and *Me* β -hydroxy- β -benzoyl- β -phenyl- α -methylpropionate, m.p. 83°; dehydration of the latter with KHSO_4 and hydrolysis of the resultant ester with $\text{KOH}\cdot\text{EtOH}$ gives (I). *cyclo*Hexene and $\text{EtCOCl}\cdot\text{SnCl}_4$ in CS_2 at -10° afford 1-propionylcyclohexene (II), b.p. 101—102°/14 mm. (oxime, m.p. 78°; semicarbazone, m.p. 189°). $\text{CH}_2\text{Ph}\cdot\text{COMe}$ gives (Reformatsky) Et β -hydroxy- β -benzyl-*n*-butyrate, b.p. 160—165°/15 mm. (corresponding *Me* ester, b.p. 151—152°/15 mm.), which with KHSO_4 at 180° for 4 hr. gives an unsaturated *Et* ester, b.p. 155—157°/14 mm. (*Me* ester, b.p. 140—141°/14 mm.), reduced slowly (H_2 , Pd-C, EtOH, atm. pressure) to *Et* β -benzyl-*n*-butyrate, b.p. 133°/12 mm. This and $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 100° (bath)/2 hr. give 1-keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 138°/11 mm. (semicarbazone, new m.p. 189°; 2 : 4-dinitrophenylhydrazone, m.p. 242°), the Na derivative (prep. with NaNH_2 in Et_2O) of which with (II) and 1-acetylcyclohexene in Et_2O gives 2-keto-1 : 10-dimethyl- (III), m.p. 104°, and 2-keto-10-methyl- (IV), m.p. 132°, -2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11-decahydrochrysene, respectively; in the prep. of (IV), an isomeride, m.p. 165°, is obtained. (III) does not give a semicarbazone, but affords a 2 : 4-dinitrophenylhydrazone. (IV) gives a semicarbazone, m.p. 227°, and a 2 : 4-dinitrophenylhydrazone, m.p. 210°. (III) and (IV) are reduced (Clemmensen) to unsaturated products, converted by Se at 280—360° into chrysene and a little of a methylchrysene, m.p. 151° [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 184—185°; unstable picrate, m.p. 162°]. A. T. P.

Synthesis of mescaline. H. JENSCH (Med. u. Chem., 1936, 3, 408—411; Chem. Zentr., 1937, i, 881).—Contrary to Hahn (A., 1934, 886) the synthesis of mescaline (β -3 : 4 : 5-trimethoxyphenylethylamine) (I) according to G.P. 526,172 is suitable for laboratory use as only the prep. of 3 : 4 : 5-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CH}_2\cdot\text{CN}$ (II) from the chloride gives >60% yield, and syringal alcohol is a readily accessible starting material. Reduction (Ni) of (II) yields (I) and *di*- β -trimethoxyphenylethylamine; hydrolysis affords 3 : 4 : 5-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. β -3 : 5-Dimethoxy-4-butoxyphenylethylamine (hydrochloride, m.p. 153°) and 6 : 7 : 8-trimethoxy-3 : 4-dihydroisoquinoline methochloride (base, m.p. 97—98°) [from (I)] are described. A. H. C.

Reactions of isomeric nitroanilines with hydrogen peroxide in hydrochloric acid solution. R. GARZULY-JANKE (Magyar Chem. Fol., 1936, 42, 169—172; Chem. Zentr., 1937, i, 3479).— $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (I) undergo nuclear chlorination when treated with 80% H_2O_2 in EtOH-conc. HCl at 30—40°; prolonged reaction also affords $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N})_2$ (II). Possible intermediates are $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NCl}_2$; these can rearrange and react with (I) [to give (II)]. 4 : 6-Dichloro-2-, m.p. 101°, 2 : 6-dichloro-4-, m.p. 191°, and 2 : 4 : 6-trichloro-3-, m.p. 98°, -nitroanilines, and 4 : 6-di-

chloro-o-, m.p. 60°, and 2 : 6-dichloro-p-, m.p. 123°-phenylenediamines appear to be new. H. B.

Reactivities and basic strengths of *p*-alkyldimethylanilines.—See A., 1939, I, 25.

Rearrangement of 1-naphthylhydroxylamine. O. NEUNHOEFFER and H. G. LIEBICH (Ber., 1938, 71, [B], 2247—2249).— $1\cdot\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{OH}$ (I) is almost quantitatively obtained by reduction of $1\cdot\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ by solid $(\text{NH}_4)_2\text{S}$ and saturated $\text{NH}_3\cdot\text{EtOH}$ at 0°. Under varied conditions of temp. and concn. it is resinated by H_2SO_4 . In 70% EtOH it is transformed by 20% H_2SO_4 into 4 : 1-OEt $\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (sulphate, m.p. 240°). Gradual addition of (I) in COMe_2 to 17% H_2SO_4 at 55° gives 1 : 4-OH $\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ in 77% yield. H. W.

Fluorene compounds. Nitrogen derivatives. F. E. RAY and G. RIEVESCHL, jun. (J. Amer. Chem. Soc., 1938, 60, 2675—2677).—2-Aminofluorene hydrochloride and COCl_2 in PhMe give 2-carbimidofluorene (I), m.p. 69—70°, converted by the appropriate alcohol into *Me*, m.p. 118°, *Et*, m.p. 121—122°, and *Pr* 2-fluorenylcarbamate, m.p. 113°, by $\text{NH}_3\cdot\text{Et}_2\text{O}$ into 2-fluorenylcarbamide, m.p. >360°, by NH_2Ph into *s*-phenyl-2-fluorenylcarbamide, m.p. 305° (block), and by 2-aminofluorene (II) into *s*-di-2-fluorenylcarbamide, m.p. >360°, which is also obtained from (II) by COCl_2 or from (I) by H_2O . 2-Benzoylfluorene, *iso*- $\text{C}_5\text{H}_7\cdot\text{O}\cdot\text{NO}$, and KOMe in a little MeOH in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ give the α -, m.p. 213—214° (acetate, m.p. 144—145°), and β -, m.p. 207—208° (acetate, m.p. 150—151°), forms of 2-benzoyl-9-fluorenoneoxime. The β -form was obtained by Fortner's method (A., 1903, i, 177), but his compound, m.p. 199°, was a 1 : 1 mixture of the two forms. R. S. C.

Preparation of thiocarbamides and thiuram disulphides. H. S. FRY and B. S. FARQUHAR (Rec. trav. chim., 1938, 57, 1223—1233; cf. A., 1934, 60).—The method of prep. of thiocarbamides and thiuram disulphides from primary and *sec.* amines, respectively, CS_2 , I, and $\text{C}_5\text{H}_5\text{N}$ (*loc. cit.*) is re-examined for extent of completion and effect of substituents. The use of 100% excess of $\text{C}_5\text{H}_5\text{N}$ usually gives quick and good results. The times required for the conversion of $\text{C}_6\text{H}_4\text{Hal}\cdot\text{NH}_2$ into $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Hal})_2$ are in the order : *o*-Br > *o*-Cl > *m*-Cl > *m*-Br > *p*-Cl > *p*-Br, *p*-1 (almost instantaneous); all except *o*-Br give yields >92%. Conversion of *sec.* amines into thiuram disulphides is fast with NHPhMe (0.33 hr.; 92% conversion) and slower with NHPhEt (11.5 hr.; 97%); NHPh_2 gives only 20% conversion in 10 weeks. Conversion of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$ (1.5 hr.; 86%) occurs more readily than the *m*- (2 hr.; 62%) and *o*- (12.5 hr.; 93%) isomerides. Unlike *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$ (3 hr.; 83%), the *o*- and *p*-isomerides do not react. The following are described : *s*-di-*o*-chloro-, new m.p. 131.5°, -*o*-bromo-, new m.p. 154°, -*m*-bromo-, new m.p. 132°, and -*p*-iodo-, m.p. 188—189° (decomp.), -phenylthiocarbamides; *tetraphenyl*-, m.p. 217.6° (decomp.), *di*-*o*-, m.p. 200.2°, -*m*-, m.p. 170.5°, and -*p*-tolyl-, m.p. 183° (decomp.), and *di*-*m*-nitrophenyl-, m.p. 172° (decomp.), -dimethylthiuram disulphides. PhNCS and *o*-, *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$ afford *N*-phenyl-*N'*-methyl-*N'*-*o*-, m.p. 89—90°, -*m*-, m.p. 67.6—

67°, and -p-, m.p. 89.4°, *-tolylthiocarbamides*, respectively. A. T. P.

Guanidine structure and hypoglycaemia. Carbocyclic diguanidines. C. E. BRAUN, J. D. ERIT, and G. C. CROOKS (J. Org. Chem., 1938, 3, 146—152).—*p*-C₆H₄(NH₂·HCl)₂ and NH₂·CN in abs. EtOH give *p*-diguanidinobenzene (I), m.p. 258—259° (decomp.) [*dihydrochloride*, m.p. 315°; *picrate*, m.p. >317° (darkens at 290°)]. (*p*-C₆H₄·NH₂·HCl)₂ and CH₂(C₆H₄·NH₂·HCl)₂ similarly give 4:4'-diguanidinodiphenyl (II), m.p. 234—236° (decomp.) [*picrate*, decomp. 308°; *dihydrochloride*, m.p. >300°; *sulphate*, m.p. 318—320° (decomp.)], and *di*-(*p*-guanidinophenyl)methane (III), m.p. 199—200° (decomp.) [*picrate*, m.p. 229—230° (darkens at 200—202°); *sulphate*, m.p. 254—256° (decomp.)]. *p*-Bromo-, m.p. 121—123° [*hydrochloride*, m.p. 175°; *carbonate*, m.p. 145—149° (decomp.)], and *p*-iodo-phenylguanidine (*carbonate*, m.p. 147—149°; *picrate*, m.p. 235°; *hydrochloride*, m.p. 151—153°), similarly prepared, could not be converted (Ullmann reaction) into (II). (I), (II), and (III) possess less hypoglycaemic activity than [CH₂]₆[N·C(NH)·NH₂]₂, and (II) and (III) are much more toxic. R. S. C.

Thermal persistence of crystalline liquid phases. C. WEYGAND and R. GABLER (Ber., 1938, 71, [B], 2399—2403).—Only very small differences exist between the groups ·N(O)·N·, ·N·N· and ·CH·N· in their action on the existence of cryst. liquid phases if attention is paid to cryst. solid phases when the strength of the cryst. liquid properties is estimated. Apparently their common factor, the double linking, is of outstanding importance for the occurrence of cryst. liquid phases. The actual series of persistencies is that of mol. wts. not only qualitatively but nearly quantitatively. The clearing temp. of the azoxy-series differ more from those of the azo-series than do the latter from those of the azomethine series, corresponding with the difference of 16 mol. wt. units between the first two and of 1 unit between the second and third. The persistent differences between the three series can therefore be referred to the same causes as the differences in m.p. observed in morphologically comparable homologous series (chloride, bromide, and iodide of higher alcohols), that is, as a first approximation, to the inertia of the different heavy individual mols. The following are described incidentally: *p*-nitrophenyl Bu^a, b.p. 160—163°/7 mm., m.p. 31—32° (from *p*-NO₂·C₆H₄·OK and Bu^aBr in EtOH at 170—190°), and *n*-amyl ether, b.p. 162—163°/5 mm. 4:4'-Dibutoxy-, m.p. 134°, and 4:4'-diamyloxy-azoxybenzene, m.p. 81—82° (turbid), clear at 119°, are obtained by electrolytic reduction (Pb cathode and Ni anode in 96% EtOH saturated with NaOAc) of the NO₂-ethers. Further reduction to the azo-stage is not secured under more drastic conditions. 4:4'-Dibutoxy-, m.p. 135°, and 4:4'-diamyloxy-azobenzene, m.p. 112°, are obtained from the (OH)₂-derivative, KOH, and the requisite alkyl iodide in boiling MeOH. H. W.

Spectrochemical study of complex colouring matters. I. Metallic complexes of 2:2'-dihydroxyazobenzene. T. UÉMURA and Y. INAMURA (Bull. Chem. Soc. Japan, 1938, 13, 623—630).—

(*o*-OH·C₆H₄·N⁺)₂ (I) and some salts of Cr, Co, and Ni in aq. KOH give the complexes, [CrR₂(H₂O)₂]₂K₂·2H₂O, [CoR₂(H₂O)₂]₂K₂, and [NiR₂(H₂O)₂]₂K₂·3H₂O (R = C₁₂H₈O₂N₂). The absorption spectra, in aq. and H₂SO₄ solutions, indicate that in the latter, the complexes undergo decomp. to (I) and metallic sulphates. The absorption curves indicate a ratio 1:2 of the metal to (I) in the new complexes.

W. R. A.

Phenols from cornstalk alkali-lignin.—See B., 1938, 1389.

Physico-chemical study of reactions in organic solution.—See A., 1939, I, 26.

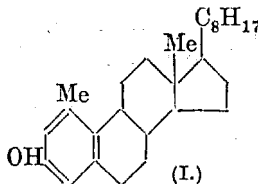
Hydroxy-by-products in aromatic nitration. G. M. BENNETT and P. V. YOUNG (J.C.S., 1938, 1816—1818; cf. A., 1938, II, 401).—Literature on the formation of OH-by-products during aromatic nitration is reviewed, and new cases are also examined. Mechanisms are discussed and it is concluded that the by-products (much larger with *m*-directing substituents) are derived from OH-compounds in which OH enters the mol. according to the normal orientation law; polynitration then occurs, and in some cases the original substituent is lost, to yield the final by-product. C₆H₆ and 96% H₂SO₄·HNO₃ (*d* 1.42) at 65° afford 2:4:1-(NO₂)₃C₆H₃·OH (0.03%); PhMe gives 3:5-dinitro-*p*-cresol (0.7%). PhNO₂ and HNO₃ (*d* 1.42, 1.52, with or without H₂SO₄) or KNO₃·H₂SO₄ give, through *m*-NO₂·C₆H₄·OH and 2:3:4:6:1-(NO₂)₅C₆H₃·OH, small amounts of styphnic acid (max. yield 5.5—6.5% by KNO₃·H₂SO₄ at 90° for 2 hr.). PhSO₂Cl affords (cf. *ibid.*, 313) 2:4:6-trinitro-3-hydroxybenzenesulphonyl chloride (1.7%); PhSO₂Me (KNO₃·H₂SO₄) and Ph₂SO₂ [HNO₃ (*d* 1.52) at 90°] give styphnic acid (1.3 and 2.2%, respectively). Nitrations catalysed by Hg must be considered independently (cf. Davis *et al.*, A., 1921, i, 338).

A. T. P.

Hydroxy- and methoxy-phenyldihydroanthracenes. F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1938, 60, 2636—2638).—9:9-Diphenyl-10-anthrone (in C₆H₆) and *p*-OMe·C₆H₄·MgI (in Et₂O) give 10-hydroxy-9:9-diphenyl-10-*p*-anisyl-9:10-dihydroanthracene, m.p. 142—144°, which with HCl-MeOH gives the 10-*OMe*-compound, m.p. 191—193°, and with PhOH or PhOMe and a little H₂SO₄ at 100° gives 9:9-diphenyl-10-*p*-hydroxyphenyl-10-*p*-anisyl-(I), m.p. 250—252°, and 9:9-diphenyl-10-*di*-*p*-anisyl-9:10-dihydroanthracene (II), m.p. 233—235°, respectively. With HBr (I) yields 9:9-diphenyl-10:10-*di*-*p*-hydroxyphenyl-9:10-dihydroanthracene, m.p. 343—345° [(*m*-C₆H₄Br·CO)₂ derivative, m.p. 231—233°], which with Me₂SO₄ gives (II) [also obtained from (I) by Me₂SO₄]. 9:9-Di-*p*-hydroxyphenylanthrone and Me₂SO₄ give 9-*p*-hydroxyphenyl-9-*p*-anisyl-, m.p. 232—233° (also obtained from 9-hydroxy-9-*p*-anisyl-10-anthrone, PhOH, and H₂SO₄), and 9:9-di-*p*-anisyl-10-anthrone (III). With *p*-OMe·C₆H₄·MgI, (III) gives 10-hydroxy-9:9:10-*tri*-*p*-anisyl-9:10-dihydroanthracene (IV), m.p. 226—228° (*Me ether*, m.p. 205—206°), converted by PhOH and H₂SO₄ into 9-*p*-hydroxyphenyl-9:10:10-*tri*-*p*-anisyl-9:10-dihydroanthracene, m.p. 310—312°, which with HBr and Me₂SO₄ yields 9:9:10:10-*tetra*-*p*-hydroxy-

phenyl, m.p. 371—374° [(m-C₆H₄BrCO)₄ derivative, m.p. 163—168°], and *-tetra-p-anisyl-9:10-dihydroanthracene*, m.p. 329—331° [also obtained from (IV) by PhOMe and H₂SO₄], respectively. R. S. C.

Conversion of sterols into aromatic compounds. III. Aromatisation of Δ^{1:4}-cholestadien-3-one. H. H. INHOFFEN and HUANG-MINLON (Naturwiss., 1938, 26, 756; cf. A., 1937, II, 147).—Δ^{1:4}-Cholestadien-3-one with Ac₂O and H₂SO₄ yields a *phenol*, m.p. 145·5° [probably (I)] [dinitrobenzoate, m.p. 178°; benzeneazo-, m.p. 182°, and Br₂-derivative (II), m.p. 83—84°; *Me ether*, m.p. 104·5—105°]. The formula (I)



is supported by the fact that (II) couples with PhN₂Cl, indicating two free *o*-positions in (I).

J. D. R.

Reaction of aliphatic olefines with thiophenol. V. N. IPATIEV, H. PINES, and B. S. FRIEDMAN (J. Amer. Chem. Soc., 1938, 60, 2731—2734).—Olefines add "abnormally" to thiophenols at 50—120° alone or in presence of H₃PO₄, but according to Markovnikov's rule in presence of H₂SO₄. CHPr^β:CH₂ is isomerised during the latter reaction, giving the *tert*-amyl product. Thus are obtained *Ph Pr^α*, b.p. 218·5—219·5°/750 mm., *Pr^β*, b.p. 206·5—207·5°/750 mm., *Bu^α*, b.p. 94·5—97°/4 mm. [PdCl₂ compound, m.p. 106—106·5° (lit., 118°)], *Bu^β*, b.p. 107—108°/13 mm. [PdCl₂ compound, m.p. 92·5—93·5° (lit., 96°)], *Bu^γ*, b.p. 73°/5 mm. (PdCl₂ compound, m.p. 84° and >250° when recryst.; *sulphone*, m.p. 98—99°), *n*-, b.p. 117—118°/8 mm. (PdCl₂ compound, m.p. 75—76°), and *iso-amyl*, b.p. 100—100·5°/6 mm. (PdCl₂ compound, m.p. 96—97°), *CHMePr^β* (I), b.p. 99—100°/5 mm., and *CMe₂Et sulphide* (II), b.p. 91—91·5°/6 mm. [*sulphone*, m.p. 29—30°; PdCl₂ compound, m.p. 72—73° and >250° when recryst.]. Structures are proved by prep. also from PhSNa and AlkBr, except that (II) could not be thus obtained; this method gives also *Ph sec*-, *Bu*, b.p. 90—91°/4 mm., *CHMePr^α*, b.p. 91—92·5°/4·5 mm., *CHEt₂*, b.p. 107—107·5°/9 mm., and active *amyl sulphide*, b.p. 99—101°/4·5 mm. *m*-Nitrophenyl *n*-, m.p. 78·5—79°, and *iso*-propyl *sulphone*, m.p. 112—113°, and *m*-aminophenyl *α*-methylisobutyl *sulphone*, m.p. 93—94°, are incidentally prepared. The compound, termed (I) by Posner (A., 1905, i, 279) was really (II), and his PhSO₂·CMe₂Et was really PhSO₂H. R. S. C.

Unsymmetrical aryl sulphides. N. E. FOSS, J. J. STEHLE, H. M. SHUSETT, and D. HADBURG (J. Amer. Chem. Soc., 1938, 60, 2729—2730).—(m-NO₂·C₆H₄·S)₂ (prep. from m-NO₂·C₆H₄·SO₂Cl by HI) and Cl₂ give m-NO₂·C₆H₄·SCL, which with the appropriate phenol gives *m*-nitrophenyl *p*-hydroxyphenyl, m.p. 83—83·5° (*Ac*, m.p. 66—67°, *Br₂*, m.p. 136—137°, *Bz*, m.p. 102—102·5°, and O-CH₂Ph derivative, m.p. 105—106°), 2:4-dihydroxyphenyl, m.p. 150·5—151·5° (*Ac₂*, m.p. 77—78°, and *Br₂*-derivative, m.p. 128—130°), and 2-hydroxy-1-naphthyl *sulphide*, m.p. 106° (*Ac*, m.p. 85—85·5°, *Bz*, m.p. 110—110·5°, and O-CH₂Ph derivative, m.p. 136—137°), and 2:4-dihydroxy-1:3-phenylene bis-(*m*-nitro-

phenyl sulphide), m.p. 179—180° (*Ac₂*, m.p. 109·5—110·5°, and *Br*-derivative, m.p. 189—190°). Hydrogenation (PtO₂) gives *m*-aminophenyl *p*-hydroxyphenyl, m.p. 84—84·5°, and 2-hydroxy-1-naphthyl *sulphide*, m.p. 193° (ON-*Ac₂* derivative, m.p. 163—164°).

R. S. C.

Cumyl alcohol. R. G. COOKE, D. T. GILLESPIE, and A. K. MACBETH (J.C.S., 1938, 1825—1826).—*p*-C₆H₄Pr^β·CH₂·OH (I), b.p. 91°/0·7 mm. (*p*-nitro-, m.p. 39—39·5°, and 3:5-dinitro-, m.p. 107°, -benzoates; phenyl-, m.p. 62°, and *α*-naphthyl-, m.p. 112—112·5°, -urethanes; *H phthalate*, m.p. 61—62°), is best prepared (70% yield) by reduction [II₂ (1340 lb.), Cu-Ba-Cr oxide catalyst, EtOH, 120°] of *p*-C₆H₄Pr^β·CHO (II). A cross-Cannizzaro reaction with (II) and CH₂O gave 42% of (I). A. T. P.

Reactions of αβ-unsaturated cyclic aldehydes and ketones. III. Reduction of cryptone. *cis*- and *trans*-dihydrocryptol. D. T. C. GILLESPIE, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1938, 1820—1824).—Reduction (Ponndorf, Al-Pr^βOH) of cryptone affords *l*-cryptol (*l*-4-isopropyl-Δ²-cyclohexen-1-ol) (I), b.p. 82—83°/2 mm., [α]_D²⁰ -45·4° (phenyl-, m.p. 105°, and *α*-naphthyl-, m.p. 118°, -urethanes), which when purified through the *p*-nitrobenzoate is stereochemically pure and has b.p. 72°/2 mm., [α]_D²⁰ -133° (homogeneous), -142° in EtOH. It is dehydrated by KIISO₄ at 120° to *l*-1-isopropyl-Δ^{2:4}-cyclohexadiene (II), b.p. 30°/4 mm., which with maleic anhydride in Et₂O forms an adduct, m.p. 133°, [α]_D²⁰ -29·16° in CHCl₃. (II) and KMnO₄·H₂O·COMe₂, then PbO₂ in dil. H₂SO₄, give isopropylsuccinic acid. Reduction of either of the above *l*-cryptols with Pd-C-EtOH affords dihydrocryptol (III) (4-isopropylcyclohexan-1-ol), b.p. 84—85°/5 mm. (*p*-nitrobenzoate, m.p. 75·5°; 3:5-dinitrobenzoate, m.p. 124·5°; phenylurethane, m.p. 114°; *α*-naphthylurethane, m.p. 159·5°), converted by *o*-C₆H₄(CO)₂O at 110° for 15 hr. into a *H phthalate*, m.p. 115°. (III) is obtained also by Ponndorf reduction of dihydrocryptone. Electrolytic reduction (Pt anode, Ni cathode) of cryptone in 95% EtOH-NiSO₄-10% H₂SO₄ at 34—36°, gives an isomeric (*cis*- or *trans*-)dihydrocryptol (IV), b.p. 60°/1·9 mm. (*p*-nitrobenzoate, m.p. 69·5°; 3:5-dinitrobenzoate, m.p. 112°; phenylurethane, m.p. 87—88°; *α*-naphthylurethane, m.p. 113°; *H phthalate*, m.p. 129°). Both (III) and (IV) are oxidised (K₂Cr₂O₇·H₂SO₄ at 30°) to dihydrocryptone (cf. A., 1937, II, 345). A. T. P.

Derivatives of 4-spiroheptane [cyclobutane-spirocyclobutane] identically substituted in the 2:6 [3:3']-positions. H. J. BACKER and H. G. KEMPER (Rec. trav. chim., 1938, 57, 1249—1258; cf. A., 1938, II, 324).—cyclobutanespirocyclobutane-3:3'-dicarboxylic acid (I) gives the *dichloride* (II), b.p. 158—160°/15 mm., converted by PhOH in boiling C₆H₅N-CHCl₃ into the *Ph₂* ester, m.p. 96—96·5°, of (I), which is reduced (Na-EtOH) to 3:3'-bis(hydroxymethyl)cyclobutanespirocyclobutane, m.p. 167°/16 mm. The *di-H phthalate*, m.p. 139—139·5°, is resolved through the brucine or neutral strychnine salt. The Me₂ ester, m.p. 14°, b.p. 141°/11 mm., of (I), with MgMeI affords 3:3'-bis-(*α*-hydroxyisopropyl)-, m.p. 75—76°, and with MgPhBr gives 3:3'-bis-(*α*-hydroxy-



*benzhydryl*cyclobutanespirocyclobutane (III), m.p. 105—105.5° (+2C₆H₅N), ~56° (decomp.) (+2Et₂O) (cryst. form examined), and 138.5—139° ("anhyd."). (III) is dehydrated (AcOH—I) to the 3 : 3'-*bisdiphenylmethylene* derivative, m.p. 116—116.5°, oxidised (O₃-AcOH) to CPh₂ and a compound, C₁₀H₁₈O₃, m.p. 190—190.5°. (II) and AlCl₃-CS₂-C₆H₆ afford 3 : 3'-*dibenzoylcyclobutanespirocyclobutane*, m.p. 73.5—74°, b.p. 263°/6 mm. [converted by MgPhBr into (III)], which does not react with HCN-C₆H₅N. A. T. P.

Oxidising action of selenium dioxide. Oxidation of acenaphthene. (SIGNA.) L. MONTI (Gazzetta, 1938, 68, 608—612).—Acenaphthene with SeO₂ at 150—170° gives acenaphthylene (15—25%) and *cis*- and *trans*-acenaphthylene glycol (cf. A., 1938, II, 138) (15—16%). E. W. W.

Interaction of β-hydroxyethylamine and halogenonitrobenzenes. K. F. WALDKÖTTER (Rec. trav. chim., 1938, 57, 1294—1310).—NH₂[CH₂]₂OH (I) reacts with halogenonitrobenzenes with elimination of labile group(s) to form derivatives of β-hydroxyethylaniline. (I) with 1 : 2 : 4-C₆H₃Cl(NO₂)₂ and picryl chloride (±NaOAc), in EtOH, gives respectively 2 : 4-dinitro- (II), new m.p. 90° (N-Ac derivative, m.p. 130°), and 2 : 4 : 6-trinitro- (III), m.p. 110° (ON-Ac₂ derivative, m.p. 117°). β-hydroxyethylanilines. (II) or (III) in abs. HNO₃ at -15° gives N-nitro-N'-2 : 4 : 6-trinitrophenyl-β-aminoethyl nitrate ["pentryl"], m.p. 129° or >188° (block), ignites at 250°. (I) and 1 : 4 : 2-C₆H₃Cl₂NO₂ in EtOH at 140—145° for 5 hr. give 4-chloro-2-nitro-β-hydroxyethylaniline, m.p. 107° (Ac₂ derivative, m.p. 48°), converted by HNO₃ at -15° into N-nitro-N-4-chloro-2 : 6-dinitrophenyl-β-aminoethyl nitrate (IV), forms, m.p. 81° (? 84°) and 92° (block), decomp. 105°, ignites 296°. (I) and 4-chloro-2 : 6-dinitroanisole in boiling EtOH give 4-chloro-2 : 6-dinitro-β-hydroxyethylaniline, m.p. 102°, which with HNO₃ yields (IV). 4-Bromo-2-nitro-, m.p. 106° (Ac₂ derivative, m.p. 53°), and 4-bromo-2 : 6-dinitro-, m.p. 114°, β-hydroxyethylanilines are similarly prepared; they are both nitrated to N-nitro-N-4-bromo-2 : 6-dinitrophenyl-β-aminoethyl nitrate, m.p. 95°, decomp. 180°, ignites 256°. (I) and 1 : 3 : 4-C₆H₃Cl(NO₂)₂ in EtOH afford 5-chloro-2-nitro-β-hydroxyethylaniline, m.p. 116° (Ac₂ derivative, m.p. 94°), which with HNO₃ at -10° gives N-nitro-N-5-chloro-2 : 4-dinitrophenyl-β-aminoethyl nitrate (V), decomp. 180°, ignites 253°, also formed similarly from 5-chloro-2 : 4-dinitro-β-hydroxyethylaniline, forms, m.p. 132° and 116° (Ac₂ derivative, m.p. 96°). 5-Bromo-2-nitro-β-hydroxyethylaniline, m.p. 126° (Ac₂ derivative, m.p. 75°, hydrolysed by boiling H₂O to the N-Ac derivative, m.p. 109°), and HNO₃ at -10° give N-nitro-N-5-bromo-2 : 4-dinitrophenyl-β-aminoethyl nitrate (VI), m.p. 114°, decomp. 173°, ignites 262°. (I) (4 equivs.) and 1 : 3 : 4 : 6-C₆H₂Cl₂(NO₂)₂ afford 4 : 6-dinitro-1 : 3-bis-(β-hydroxyethylamino)benzene, m.p. 211° [NN'-Ac₂ derivative, m.p. 149°; (?) 2 : NN'-(NO₂)₃ derivative, decomp. violently at 98°, ignites at 230°]. Equiv. amounts of (I) and 1 : 3 : 4 : 5-C₆H₃Cl₂(NO₂)₂ in EtOH (3 hr.) give 4 : 6-dichloro-2-nitro-β-hydroxyethylaniline, m.p. 51° (Ac₂ derivative, m.p. 82°), whence N-nitro-N-4 : 6-dichloro-2-nitrophenyl-β-aminoethyl nitrate, m.p. 88°,

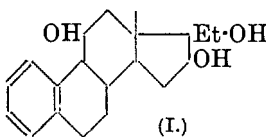
decomp. 187°, ignites 305°. 4 : 6-Dibromo-2-nitro-β-hydroxyethylaniline, m.p. 71° (Ac₂ derivative, m.p. 86°), and HNO₃ yield N-nitro-N-4 : 6-dibromo-2-nitrophenyl-β-aminoethyl nitrate, m.p. 69°, decomp. 178°, ignites 305°. (V) and (VI) with EtOH-NH₂Ph appear to give the same (?) 5-NHPh-derivative, m.p. ~60°. A. T. P.

Diaryl(dimethylaminomethyl)carbinols.—See B., 1938, 1502.

Quantitative measurement of the ultra-violet activation of sterols. I. Ergosterol. R. S. HARRIS, J. W. M. BUNKER, and L. M. MOSHER (J. Amer. Chem. Soc., 1938, 60, 2579—2580).—Activation (measured biologically) of ergosterol in Et₂O is α the quanta of energy absorbed (not the ergs) and equal for light of 2537, 2652, 2804, 2967, or 3205 Å. Possibly, however, 2804 is the most effective λ.

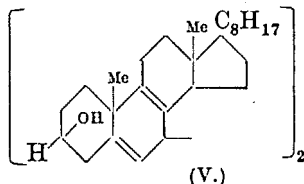
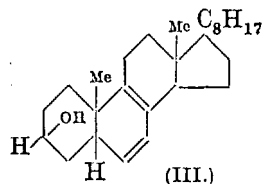
R. S. C.

Coffee. IV. Elucidation of the constitution of cafesterol. K. H. SLOTTA and K. NEISSER (Ber., 1938, 71, [B], 2342—2346).—The formula C₂₀H₂₈O₃ is confirmed for cafesterol (I) by the examination of its monoacetate (II), m.p. 163.5—165°, [α]_D²⁰ -134.6° in CHCl₃, obtained by use of NaOAc and boiling Ac₂O. More drastic conditions do not lead to a more highly acetylated product so that only 1 O of (I) is present as acetylable primary or *sec.* OH. CO and phenolic OH are absent. One of the outstanding O atoms must be present in a *tert.* OH group vicinal to the acetylable OH since Zn dust transforms (I) or (II) at 160—190°/0.01 mm. into anhydrocafesteryl (III), m.p. 126—128° [semicarbazone, m.p. 227—229° (decomp.)]. The nature of the third O could not be elucidated and its presence is suggested as an unreactive *sec.*-OH such as has been proved present in corticosterone. (II) is very rapidly hydrogenated (PtO₂) to hexahydrocafesteryl acetate, m.p. 101—105° (among other compounds). The three double linkings appear equiv.; they cannot be saturated with Na and EtOH and therefore are not present in an aliphatic conjugated system; hence one ring is probably aromatic. Hydrogenation (PtO₂ in AcOH) of (III) yields octahydroanhydrocafesteryl. (I) has probably the structure shown. Further examination shows substance A (A., 1938, II, 449) to be a mixture (1 : 1) of (I) and γ-sitosterol. Substance S is probably a paraffin alcohol not closely related to (I). Substance I, C₂₇H₄₈O, is nearly allied to the true sterols; it cannot be acetylated and does not react with NH₂·CO·NH·NH₂. H. W.



Product of the irradiation of Δ^{6:8}-cholestadienol. A. WINDAUS and G. ZÜHLSDORFF (Annalen, 1938, 536, 204—216; cf. A., 1938, II, 185).—The first preparatively established, photochemical transformation product of Δ^{6:8}-cholestadienol (I) is due to a steric rearrangement at C₁₅, which corresponds exactly with the first photochemical transformation of Δ^{6:7}-cholestadienol (II) at C₁₀, since in accordance with the rule of double linkings the union between C₁₅ and C₁₀ in (I) is loosened in the same manner as that between C₁₀ and C₁₁ in (II). Exposure of (I) in pure C₆H₆ to a Mg spark light leads to Δ^{6:8}.

coprostadienol (III), m.p. 92° [acetate (IV), m.p. 101°, $[\alpha]_D^{20} +176.5^\circ$ in CHCl_3 ; benzoate, m.p. 125°, $[\alpha]_D^{20}$



+167° in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 192°, $[\alpha]_D^{20} +127^\circ$ in CHCl_3], which gives a sparingly sol. additive compound with digitonin and strongly resembles (I) in its absorption spectrum, indicating the presence of conjugated double linkings in a ring. This view is confirmed by the isolation of an adduct, $\text{C}_{33}\text{H}_{48}\text{O}_5$, m.p. 242—244°, $[\alpha]_D^{25} +47.3^\circ$ in CHCl_3 , from (IV) and maleic anhydride, and by oxidation $[\text{HNO}_3 (d\ 1.4)]$ of (III) to $\text{C}_6\text{HMe}(\text{CO}_2\text{H})_4$. Photochemical dehydrogenation of (I), (II), or (III) in presence of eosin gives the dihydric alcohol (V), [diacetate (VI), m.p. 202° (decomp.), $[\alpha]_D^{20} -133.5^\circ$ in CHCl_3 ; dipropionate, m.p. 197° (decomp.), $[\alpha]_D^{20} -125.5^\circ$; diisobutyrate, m.p. 184—185°, $[\alpha]_D^{20} -114.5^\circ$]. (VI) is transformed by hot Ac_2O into the norsteryl acetate $\text{C}_{26}\text{H}_{39}\text{OAc}$ (corresponding dinitrobenzoate, m.p. 207°, $[\alpha]_D^{25} +2.5^\circ$ in CHCl_3). Hydrogenation (Pt sponge in AcOH) at room temp. and, after addition of conc. HCl , at 60° of (IV) yields coprosteryl acetate, m.p. 88—90° (corresponding dinitrobenzoate, m.p. 214—215°). Oxidation of (IV) with BzO_2H in CHCl_3 gives unidentified crystals, m.p. 73—78°, and material which is acetylated (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) to Δ^8 -coprostene-3:6:7-triol diacetate benzoate, m.p. 200—201°, $[\alpha]_D^{20} +32^\circ$ in CHCl_3 , hydrolysed to Δ^8 -coprostene-3:6:7-triol, m.p. 191—192° (triacetate, m.p. 150—151°). (III) is reduced by Na and PrOH to δ -coprostenol [$\Delta^{8,9}$ -coprostenol], m.p. 80—83°, $[\alpha]_D^{21} +15.0^\circ$ in CHCl_3 (dinitrobenzoate, m.p. 195—196°, $[\alpha]_D^{21} +33.5^\circ$ in CHCl_3); the corresponding acetate, m.p. 107—108°, $[\alpha]_D^{21} +43.5^\circ$ in CHCl_3 , is isomerised by H_2 -Pd to α -coprostenyl acetate, m.p. 114—115°, $[\alpha]_D^{25} +30.5^\circ$ in CHCl_3 (corresponding dinitrobenzoate, m.p. 181°, $[\alpha]_D^{20} +27.3^\circ$ in CHCl_3), also obtained by hydrogenation (Pd sponge in EtOAc at room temp.) of (IV). HCl and (IV) in CHCl_3 at 0° give an isomide, m.p. 80—81°, $[\alpha]_D^{19} -49.3^\circ$ in CHCl_3 , of the type of ergosterol B and containing its conjugated double linkings in two rings. It is hydrolysed to coprostadienol B, m.p. 75°, $[\alpha]_D^{20} -48^\circ$ (dinitrobenzoate, m.p. 169°). Catalytic perhydrogenation transforms it into coprosterol. When heated with maleic anhydride it is re-converted into (III). H. W.

α -Theosterol, $\text{C}_{30}\text{H}_{50}\text{O}_3$, m.p. 113—114° [acetate, m.p. 113—115°; digitonide, m.p. 222—224° (decomp.)], from cacao germ oil.—See A., 1939, III, 109.

Separation of the antirachitically acting components of irradiated 7-dehydrocholesterol.—See B., 1938, 1502.

Transmission of substituent influences in ester hydrolysis.—See A., 1939, I, 31.

Reactivity of the ω -halogen atom in *p*-alkoxybenzyl halides: preparation of phenylacetic

acids. R. G. NAIK and T. S. WHEELER (J.C.S., 1938, 1780—1783).—6-Chloro- (I) and -bromo-piperonal (II) (prepared in AcOH), and 3-chloro- (III) and -bromo- (IV) *p*-anisaldehyde with NH_2Ph at 100° give the corresponding anils, m.p. 112°, 131—132°, 85°, and 96—97°, respectively. (I), (II), (III), and (IV), with 50% aq. NaOH-EtOH at 50° (cf., Ahmad *et al.*, A., 1938, II, 337), afford 6-chloro-, m.p. 73—74°, and -bromo-, m.p. 90°, -3:4-methylenedioxybenzyl, and 3-chloro-, b.p. 178—180°/10 mm., and -bromo-, m.p. 63—64°, -4-methoxybenzyl alcohols, respectively, converted by $\text{HCl-C}_6\text{H}_6$ at 0° or $\text{HBr} (d\ 1.69)$ into 6-chloro-3:4-methylenedioxybenzyl chloride, m.p. 65°, and bromide, m.p. 75—76°; 6-bromo-3:4-methylenedioxybenzyl chloride, m.p. 64—65°, and bromide, m.p. 94° (also from 3:4-methylenedioxybenzyl alcohol or Me ether and 1 mol. of Br); 3-chloro-4-methoxybenzyl chloride (V), b.p. 145—147°/6 mm., and bromide, m.p. 52—53°; 3-bromo-4-methoxybenzyl chloride, m.p. 51—52°, and bromide, m.p. 61—62°. The chlorides and $\text{KI-COMe}_3\text{-H}_2\text{O}$ at 100° for 1½ hr. give the corresponding iodides, m.p. 95—96°, 90—91°, 61—62°, and 64—65°, respectively. The chlorides and KCN-EtOH for 24 hr. afford respectively 6-chloro-, m.p. 70—71°, and -bromo-, m.p. 71—72°, piperonylacetone nitrile, and 3-chloro-, m.p. 54—55°, and -bromo-, m.p. 56—57°. *p*-anisylacetone nitriles, hydrolysed by aq. NaOH-EtOH at 100° for 8 hr. to 6-chloro-, m.p. 174—175° (Me, m.p. 69—70°, and Et ester, m.p. 60—61°), and -bromo-, m.p. 190° (Et ester, m.p. 69—70°), piperonylacetic acid, and 3-chloro-, m.p. 95—96°, and -bromo-, m.p. 114—115°, *p*-anisylacetic acid, respectively. (V) and MeOH or EtOH at 100° for 2 hr. give 3-chloro-4-methoxybenzyl Me, b.p. 135—140°/5 mm., and Et, b.p. 150—155°/10 mm., ethers. 3-Bromo-4-methoxybenzyl Et ether boils at 155—160°/10 mm. The ethers with $\text{HCl-C}_6\text{H}_6$ or $\text{HBr} (d\ 1.69)$ are reconverted into the halides. 3:4-Methylenedioxybenzyl bromide (VI) and hot MeOH (EtOH) give 2:3:6:7-bismethylenedioxy-9:10-dihydroanthracene, m.p. >360°, but (VI) and MeOH + Na_2CO_3 at 100° for 1½ hr. afford 3:4-methylenedioxybenzyl Me ether, b.p. 120°/10 mm. (cf. Kobayashi, A., 1928, 169). The 6-halogeno-3:4-methylenedioxybenzyl halides react with alcohols without forming dihydroanthracene derivatives, but the resultant oils contain more halogen than the expected ethers; 6-nitro-3:4-methylenedioxybenzyl chloride does not react. 6-Chloro- and -bromo-3:4-methylenedioxybenzyl halides and PCl_5 at 120° for 4 hr. give the unstable 6-chloro-, b.p. 150—154°/10 mm., and -bromo-, b.p. 155—157°/10 mm., -3:4-dichloromethylenedioxybenzyl chloride (cf. Ewins, J.C.S., 1909, 95, 1482), HCO_2H then giving 6-chloro-, m.p. 64°, and -bromo-, m.p. 80—81°, -3:4-carbonyldioxybenzyl chloride, respectively. A. T. P.

Reactivity of the methylene group in derivatives of phenylacetic acid. G. D. PARKES and B. C. ALDIS (J.C.S., 1938, 1841—1845; cf. A., 1936, 1497).—The actions of HNO_2 and diazonium salts respectively on derivatives of phenylacetic acid are recorded (cf. Meyer, A., 1889, 516). The Me ester of 2:4-dinitrophenylacetic acid (I) (benzyl ester, m.p. 98°) with $p\text{-C}_6\text{H}_4\text{Hal-N}_2\text{Cl}$ or 2:4- $\text{C}_6\text{H}_3(\text{Hal})_2\text{N}_2\text{Cl}$ in NaOAc-EtOH affords respectively Me *p*-chloro-, m.p. 155°, *p*-bromo-, m.p. 182°, 2':4'-dichloro-, m.p. 181°,

and 2':4'-dibromo-, m.p. 199°, -benzeneazo-2:4-dinitrophenylacetate. Me benzeneazo-2:4-dinitrophenylacetate and Br-AcOH-NaOAc afford ω -bromo-2:4-dinitrobenzaldehyde-*p*-bromophenylhydrazone (cf. Chattaway *et al.*, A., 1931, 1416), probably through the unstable Me *p*-bromobenzeneazo-2:4-dinitrophenylacetate. (I) and PhN₂Cl-aq. NaOAc give formazyl-2:4-dinitrobenzene, 2:4:1-(NO₂)₂C₆H₃C(N:NPh):N:NHPh, m.p. 198°; similarly prepared are pp'-dibromo- (II), m.p. 220°, 2':2'':4':4'':tetra-chloro-, m.p. 206° (darkens at 150°), and -tetra-bromo-, m.p. 201° (darkens at 150°), -formazyl-2:4-dinitrobenzene, stable to boiling HCl. (II) and Sn-HCl afford 6(or 7)-bromo-3:2':4'-diaminophenyl-1:2:4-benzotriazine, m.p. 180° (darkens at 160°). (I)-aq. (NH₄)₂S-H₂S, boiled for 5-6 hr., give 2-nitro-4-aminophenylacetic acid (III), m.p. 185° [Ac (IV), m.p. 205°, and Bz, m.p. 223°, derivatives], which at 190° for a few min. gives 2-nitro-4:2'-nitro-4'-aminophenylacetamidophenylacetic acid, m.p. 213° (some 2-nitro-*p*-toluidine is formed also if reaction is at 270°) (cf. Gabriel and Meyer, A., 1881, 729). (IV) is stable to HNO₃, but with KMnO₄-MgSO₄-H₂O, refluxed for 7 hr., it gives 4:2:1-NHAc-C₆H₃(NO₂)₂-CO₂H. Diazotisation of (III) followed by CuCl affords 4-chloro-2-nitro-benzaldehyde and -phenylacetic acid; thus even in the cold, HNO₂ attacks the CH₂. (III) and Br-AcOH at 60° for a few min. give impure 5-bromo- [Ac derivative, oxidised to 4:5:2:1-NHAc-C₆H₂Br(NO₂)₂-CO₂H, m.p. 246°] and 3:5-di-bromo-2-nitro-4-aminophenylacetic acid [Ac derivative, m.p. 240° (decomp.)]. (I) does not react with HNO₃ and no reaction occurs between NO₂-C₆H₄-CH₂-CO₂H and HNO₂ or ArN₂Cl. 6-Amino-oxindole [Ac, m.p. 324° (stable to HNO₂), and Bz derivative, m.p. 273°] with C₆H₅N₃O-NHCl followed by CuCl gives 6-chloro-oximino-oxindole, m.p. 240°, and (impure) 6-chloro-oxindole. 6-Nitro-oxindole and *p*-C₆H₄Br-N₂Cl-NaOAc give 6-nitro-3-*p*-bromobenzeneazo-oxindole, m.p. 281° (decomp.) (cf. Borsche and Meyer, A., 1922, i, 53). A. T. P.

Derivatives of salicylic acid. XIII. Chloro-salicylic acids and their methyl ethers. N. W. HIRWE, K. N. RANA, and K. D. GAVANKAR (Proc. Indian Acad. Sci., 1938, 8, A, 208-213).—5-Sulpho-salicylic acid with Cl₂ in glacial AcOH or with KMnO₄ in conc. HCl, and subsequent decomp. with superheated steam, yields 3-chlorosalicylic acid (I) [K, Ca (+3H₂O), and Ag salts; amide, m.p. 174-176°], also obtained by hydrolysis of chloral-3-chlorosalicylamide, m.p. 159-160° (from chloralsalicylamide and Cl₂ in AcOH). Methylation (Me₂SO₄-KOH) of (I) yields 3-chloro-2-methoxybenzoic acid, m.p. 120-121° [Na (+H₂O), Ba (+4H₂O), and Ag salts; amide, m.p. 99-100°]. *o*-OH-C₆H₄-CO₂H in AcOH at 0° yields with 1 mol. of Cl₂, 5-chloro-, and with 2 mols. 3:5-dichloro-salicylic acid [Ca (+4H₂O) salt]. *o*-OMe-C₆H₄-CO₂H under the same conditions yields 5-chloro- (Ag salt; amide, m.p. 137-138°) and 3:5-dichloro-2-methoxybenzoic acid [Na (+2H₂O), Ba (+5H₂O), and Ag salts; amide, m.p. 152-153°]. A. Li.

Rearrangement of aryl salicylates. B. T. TOZER and S. SMILES (J.C.S., 1938, 1897-1900; cf.

A., 1936, 716).—The following are prepared from the appropriate acid by fusion at 140°, or better in boiling xylene, with *p*-NO₂-C₆H₄-OH and PCl₅: *p*-nitrophenyl 4-hydroxy-*m*-toluate (I), m.p. 136°, 2-hydroxy-*m*-toluate (II), m.p. 153°, 5-chloro-2-hydroxybenzoate (III), m.p. 164°, 2-hydroxy-3-naphthoate (IV), m.p. 164°, and 5-nitro-2-hydroxybenzoate (V), m.p. 200°. 2:4:6-Trichlorophenyl salicylate (VI), m.p. 125°, is prepared by the fusion method. *p*-Nitrophenyl salicylate and (I), (II), (III), and (IV) with boiling *N*-NaOH (1.25 mols.) for 1½ hr. afford respectively 4'-nitro-2-carboxydiphenyl ether, m.p. 161° (70% yield), *p*-nitrophenyl 3-carboxy-*p*-, m.p. 173°, and -*o*-, m.p. 143° (Me ester, m.p. 99°), -tolyl ethers, 4-chloro-4'-nitro-2-carboxydiphenyl ether, m.p. 174-175°, and *p*-nitrophenyl 3-carboxy- β -naphthyl ether, m.p. 208°. The last could not be decarboxylated. Under the above conditions, (V) and (VI) show no evidence of rearrangement. *o*-NO₂-C₆H₄-OK and *O*-carbethoxy-*p*-cresol-3-sulphonyl chloride (VII) at 100° for ½ hr. give a product, decarbethoxylated with *N*-NaOH-EtOH at 15° to *o*-nitrophenyl 4-hydroxy-toluene-3-sulphonate, m.p. 88°. This is rearranged by boiling 0.25*N*-NaOH-EtOH for ½ hr. to *o*-nitrophenyl 3-sulpho-*p*-tolyl ether, which with PCl₅ at 130° for 1 hr. gives 4-*o*-nitrophenoxytoluene-3-sulphonyl chloride, m.p. 132° (sulphanilide, m.p. 157°), also prepared from *o*-nitrophenyl 3-sulphino-*p*-tolyl ether and 6% NaOCl. (VII) and PhOH in boiling COMe₂ + K₂CO₃ form a product, decarbethoxylated to Ph 4-hydroxy-toluene-3-sulphonate, new m.p. 57° (Na derivative, m.p. 220-230°, readily sol. in cold CHCl₃). The Na derivative of Ph salicylate melts at 193-195° (cf. A., 1938, II, 320). The tendency to form covalent Na derivatives may assist the rearrangements.

A. T. P.

Stability of esters of *p*-hydroxybenzoic acid. F. REIMERS (Dansk Tidsskr. Farm., 1938, 12, 240-247).—Hydrolysis of esters of *p*-OH-C₆H₄-CO₂H (I) by alkalis can be followed by bromometric titration, the esters giving Br₂-derivatives and (I) giving 2:4:6-C₆H₂Br₃-OH (cf. A., 1938, II, 409). No hydrolysis occurs on boiling with H₂O. Na salts of esters of (I) are hydrolysed slowly on storage and rapidly in aq. solution. *Pr*^a, m.p. 106-109°, and benzyl, m.p. 109-110°, 3:5-dibromo-4-hydroxybenzoates have been prepared. M. H. M. A.

1-Amino-4-hydroxynaphthalene-8-carboxylic acid.—See B., 1938, 1390.

Reduction and autoxidation products of 7:7-di(hydroxyaryl)acenaphthenones. I. MATEI and E. BOGDAN (Ber., 1938, 71, [B], 2296-2300).—Reduction of 8-keto-7:7-di-4'-hydroxy-3'-methylphenylacenaphthene by Zn dust and NaOH under H₂ or CO₂ yields 7:7-di-4'-hydroxy-3'-methylphenylacenaphthen-8-ol (I), m.p. 117°, converted by air in the presence of alkali into the compound, 1:8-C₁₀H₆< $\frac{\text{CH(OH)}}{\text{CR}_2}$ >O (R = 4:3-OH-C₆H₃Me), m.p. 230-235° (decomp.) (dibenzoate, m.p. 230°). Exhaustive autoxidation of (I) leads to di-*o*-cresol-naphthalein, m.p. (indef.) <100°, which dissolves in alkali to an intense violet solution. Reduction of 8-keto-7:7-di-*p*-hydroxyphenylacenaphthene by Zn dust and NaOH followed by passage of air through

the solution gives *di-p-hydroxyphenyl-8-carboxy-1-naphthylcarbinol*, m.p. 239—240°. *Di-4'-hydroxy-2':5'-dimethylphenyl-*, m.p. 233° (decomp.) (*dibenzoate*, indef. m.p.), and *di-4-hydroxynaphthyl-* (*dibenzoate*, indef. m.p.) -8-carboxy-1-naphthylcarbinol are obtained analogously. H. W.

Multipplanar cyclohexane rings. R. D. DESAI, R. F. HUNTER, and G. S. SAHARIA (*Nature*, 1938, **142**, 798).—Bromination of the isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid (A., 1936, 846) gives Br₁-acids, hydrolysed (hot aq. Na₂CO₃) to the corresponding OH-acids, which are oxidised (alkaline KMnO₄) to isomeric forms of 4-methylcyclohexane-1:1-dicarboxylic acid. Similar observations have been made in the 3-methylcyclohexane series. L. S. T.

Octa- and deca-hydronaphthalene-9:10-dicarboxylic acid. P. BRIGL and R. HERRMANN (Ber., 1938, **71**, [B], 2280—2282; cf. Alder *et al.*, A., 1938, II, 491).—Butadiene and Δ¹-tetrahydronaphthalic acid at 160—170° give (after hydrolysis) octahydronaphthalene-9:10-dicarboxylic acid, m.p. 190° [anhydride, m.p. 68°; *imide*, m.p. 176°; *hydrazide*,

C₁₀H₁₄< $\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}$ >N·NH₂, m.p. 98° (*Ac* derivative, m.p. 225°)]. It is hydrogenated (PtO₂ in AcOH) to decahydronaphthalene-9:10-dicarboxylic acid (I), decomp. 192° (block) when slowly heated [anhydride, m.p. 96°; Me₂ ester, m.p. 63°; *imide*, m.p. 188—189°; *hydrazide*, m.p. 137—138° (*Ac*₁ derivative, m.p. 170°)]. The Et₂ ester, m.p. 48°, of (I), obtained from the Ag₂ salt and EtI, is transformed by very energetic hydrolysis into the *Et H* ester, m.p. 120—121°, which is very resistant towards boiling 2N-NaOH. (I) therefore resembles (CMe₂·CO₂H)₂ rather than *o*-C₆H₄(CO)₂O. H. W.

Lactone formation of the addition product of maleic anhydride and dicyclohexenyl. R. ADAMS and E. E. GRUBER (*J. Amer. Chem. Soc.*, 1938, **60**, 2792—2794).—Δ^{12:13}. Dodecahydrophenanthrene-9:10-dicarboxylic acid (I) (A., 1936, 331) or its anhydride (II) [prep. from (I) and Ac₂O] with HCl-abs. EtOH gives the *lactone*, m.p. 109—110°, of 12-hydroxy-10-carbethoxytetradecahydrophenanthrene-9-carboxylic acid, converted by 5% NaOH into Na₂ 12-hydroxytetradecahydrophenanthrene-9:10-dicarboxylate, from which acid ppts. the 9:12-*lactone-acid*, m.p. 246—247°, also obtained from (I) by hot, conc. HCl-COMe₂ or, with (II), by heating alone at 200—210°. With EtOH-NaOEt (II) gives *Et H* Δ^{12:13}. dodecahydrophenanthrene-9:10-dicarboxylate, m.p. 127—128°, hydrolysed to (I) by alkali. The unsaturated compounds, but not the lactones or Na₂ salt, absorb Br. Oily by-products are formed in all the above reactions. R. S. C.

Syntheses in the hydroaromatic series. III. (A) Further diene syntheses from 6-methoxy-1-acetylenyl- and -1-vinyl-3:4-dihydronaphthalene. (B) Condensation of cyclopentadienes with acetylene. (FRL.) E. DANE, O. HÖSS, K. EDER, J. SCHMITT, and O. SCHÖN (*Annalen*, 1938, **536**, 183—196; cf. A., 1937, II, 500).—(A) Me₂ 7-hydroxyoctahydrophenanthrene-1:2-dicarboxylate has m.p. 174—175°. The constitution of 7-methoxy-1:2:9:10-

tetrahydrophenanthrene-1:2-dicarboxylic anhydride (I) (*loc. cit.*) (free acid, new m.p. 216°) is established by its dehydrogenation (Pt-black at 280°) to 7-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p. 253—254°. *p*-Benzoquinone in boiling PhOMe converts (I) into 7-methoxy-1:2-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p. 221—221·5° (corresponding acid, m.p. 221°, and its Me₂ ester, m.p. 138°), hydrogenated (Pd-C) to the 1:2:3:4-H₄-anhydride. Similarly di-6-methoxy-3:4-dihydro-1-naphthylacetylene is transformed into di-6-methoxy-1-naphthylacetylene, m.p. 195°, hydrogenated (Pd-C in dioxan) to di-6-methoxy-1-naphthyl-ethane, m.p. 154°. 3:6-Diketo-10-methoxytetrahydrochrysene (*loc. cit.*) is hydrogenated (Pd-CaCO₃ or Pd-C in PhOMe) to 3:6-diketo-10-methoxydodecahydrochrysene (II), m.p. 130—132° or 145—148° (according to the catalyst used), which gives non-cryst. products when treated with HBr-AcOH; when reduced in presence of PtO₂ in AcOH or PhOMe it yields a *compound*, (?) C₁₅H₂₀O₂, m.p. 194° or 183—184° according to the solvent used. Hydrogenation (PtO₂ in AcOH) of (II) affords 3:6-dihydroxy-10-methoxydodecahydrochrysene, m.p. 163°, the *diacetate*, m.p. 153°, of which is transformed by HBr-AcOH into 10-methoxyoctahydrochrysene, m.p. 148—149°. Boiling Et propiolate and 6-methoxy-1-acetylenyl-3:4-dihydronaphthalene in N₂ give, after hydrolysis, re-esterification (CH₂N₂), and adsorption (Al₂O₃) 7-methoxy-9:10-dihydrophenanthrene-2-carboxylic acid, m.p. 206—207° [as Me ester (III), m.p. 86°], which does not absorb H₂ in presence of Pd-CaCO₃ or PtO₂ in cyclohexane or EtOH, and 7-methoxy-9:10-dihydrophenanthrene-1-carboxylic acid, m.p. 152—153°; the constitution of the former follows from its dehydrogenation (Se at 300°) to 7-methoxy-2-methylphenanthrene, m.p. 143—144° (whence 7-hydroxy-2-methylphenanthrene, m.p. 146°), not identical with the known 1-Me product. 7-Hydroxy-9:10-dihydrophenanthrene-2-carboxylic acid (+0·5MeOH) (*Et* ester, m.p. 146°) has m.p. 246°. *p*-Benzoquinone and (III) at 200° give Me 7-methoxyphenanthrene-2-carboxylate, m.p. 134°.

(B) *cyclo*Pentane-1:2-dione and CH₃C·MgBr yield 2-hydroxy-2-acetylenylcyclopentanone, b.p. 50°/0·1 mm., which does not give a coloration with FeCl₃ or react with dinitrophenylhydrazine. 2-Hydroxy-5-methyl-2-acetylenylcyclopentanone, b.p. 65°/0·2 mm., gives a colourless Ag derivative which rapidly becomes brown. H. W.

Benzaldehyde reaction of deoxycholic acid. T. SHIMADA (*J. Biochem. Japan*, 1938, **28**, 169—174).—Whilst free deoxycholic acid gives a green colour (A., 1938, II, 365), the conjugated acid, *e.g.*, glycodeoxycholic, produces a blue colour. The reaction indicates that the acid is conjugated in rabbit's bile and mainly free in the bile of ox and dog. Anthropol and hyo-deoxycholic acid give a violet colour with the reagent. F. O. H.

Action of concentrated hydrochloric acid on chenodeoxycholic acid. K. YAMASAKI and K. TAKAHASHI (*Z. physiol. Chem.*, 1938, **256**, 21—27; cf. A., 1938, II, 492).—Chenodeoxycholic acid with AcOH-conc. HCl gives a *hydroxycholenic acid* (I),

$C_{24}H_{38}O_3$, m.p. 185° , $[\alpha]_D^{20} +96^\circ$ in EtOH, which with PtO_2-H_2 in EtOH gives lithocholic acid (II) and β -apochenodeoxycholic acid (III), $C_{24}H_{38}O_3$, m.p. 196° , $[\alpha]_D^{20} +77^\circ$ in EtOH (acetate, m.p. 164°). (III) in a high vac. at $250-280^\circ$ for 30 min. and then at $350-360^\circ$ gives a *choladienic acid*, $C_{24}H_{36}O_2$, m.p. 163° , $[\alpha]_D +41.9^\circ$ in EtOH, which with PtO_2-H_2 in AcOH gives δ -*chenenic acid*, $C_{24}H_{38}O_2 \cdot H_2O$, m.p. 173° (decomp. 170°), $[\alpha]_D^{20} +43.6^\circ$ in EtOH. Oxidation (CrO_3 , AcOH) of (III) gives a *ketocholeonic acid*, $C_{24}H_{36}O_3$, m.p. 137° (oxime, decomp. 227°). (I) is probably a mixture of a 3-hydroxy- $\Delta^{7:8}$ -choleonic acid [reduced to (II)] and (III) (which has a double linking at 8:14 or 8:9 and is not reducible). W. McC.

Autoxidation of benzaldehyde in presence of didiphenylene-ethylene. G. WITTIG and W. LANGE (Annalen, 1938, 536, 266—284; cf. A., 1937, II, 284).—The inhibitor action of tetraphenylpolyenes towards the autoxidation of PhCHO increases with the no. of C:C linkings and the hydrocarbons, which are otherwise stable towards O_2 , become oxidised in an increasing degree. The products are, however, intractable mixtures wherefore the study is restricted to didiphenylene-ethylene (I). In non-polar solvents this is stable to light and air for months but in polar media (EtOH, Et_2O , dioxan) it is autoxidised to fluorenone (II); the change occurs very much more rapidly in presence of PhCHO. BzO_2H is not an intermediate in the change since it does not attack (I) under the experimental conditions and oxidises (I) to (II) only at $80-90^\circ$ and in presence of a large excess of BzO_2H without detectable intermediate production of the ethylene oxide. Evidence is adduced that OH or other radical is not the carrier of a chain reaction and that therefore the hypothesis of Haber and Willstätter (A., 1932, 352) must be discarded. It is considered that PhCHO first adds O_2 to a very reactive "mol. adduct" $PhCHO \cdots O=O$; this either may become stabilised to BzO_2H (which is unimportant for the further autoxidation of PhCHO) or may react with a second mol. of PhCHO with formation of 2 mols. of $BzOH$. The energy thereby liberated activates a further mol. of PhCHO which adds O_2 and continues the autoxidation as a chain reaction; the further possibility of intermediate formation of 2 equivs. of $CHPh \langle \overset{O}{\underset{O}{\rangle}}$ is suggested by the production of some $CHPh$: ether of *cis*-diphenylacenaphthylene glycol from 7:8-diphenylacenaphthylene [used instead of (I)]. If the "mol. adduct" encounters a mol. of (I) instead of PhCHO there is production of (II) whereby PhCHO is regained or formation of $BzOH$ occurs. Since the energy thus liberated is inadequate to activate a fresh mol. of PhCHO, the oxidation of 1 mol. of (I) inhibits that of a complete chain of PhCHO mols. The possibility that labile mol. adducts can evolve O in an activated form is established by the observation that, whereas dioxan is not appreciably affected by prolonged exposure to O_2 , solutions of (I) in this solvent absorb more O_2 than is required for the transformation of (I) into (II). The behaviour of autoxidising PhCHO in presence of hydrocarbons at higher concn. is thus readily explained. H. W.

Preparation of *m*-bromobenzaldehyde. F. T. TYSON (J. Amer. Chem. Soc., 1938, 60, 2821).— m - $C_6H_4Br \cdot CHO$, prepared from m - $NO_2 \cdot C_6H_4 \cdot CHO$ by $SnCl_2-HCl$ and diazotisation (Sandmeyer) (NH_2 -compound not isolated) and previously regarded as pure, contains both Cl and Br. R. S. C.

γ -Substitution in the resorcinol nucleus. I. Synthesis of γ -resorcyraldehyde. R. C. SHAH and M. C. LAIWALLA (J.C.S., 1938, 1828—1832; cf. Limaye, A., 1937, II, 258).—Me β -resorcyate and $Zn(CN)_2-AlCl_3$ in dry Et_2O-HCl give Me 2:4-dihydroxy-3-formylbenzoate (I), m.p. $138-140^\circ$ [2:4-dinitrophenylhydrazones, m.p. $291-293^\circ$ (decomp.); semicarbazone, decomp. $260-265^\circ$; oxime, m.p. $164-165^\circ$; anil, m.p. $131-132^\circ$], reduced ($Zn-Hg$, dil. $HCl-EtOH$ at 100°) to Me 2:6-dihydroxy-*m*-toluate (II), m.p. $134-135^\circ$, which is converted by $MeI-NaOMe-MeOH$ into Me 2-hydroxy-6-methoxy-*m*-toluate, new m.p. $77-79^\circ$. (I) and $CH_3(CO_2Et)_2$ in C_5H_5N -piperidine at 100° for 1 hr. give Et 5-hydroxy-6-carbomethoxycoumarin-3-carboxylate, m.p. $157-158^\circ$. (I) and $Br-AcOH$ afford Me 5-bromo-2:4-dihydroxy-3-formylbenzoate, m.p. $133-134^\circ$ (2:4-dinitrophenylhydrazones, m.p. $294-295^\circ$); $MeI-K_2CO_3-COMe_2$ yields Me 2-hydroxy-4-methoxy-3-formylbenzoate, m.p. $121-122^\circ$, whereas $Me_2SO_4-KOH-MeOH$ at 100° gives 2:4-dimethoxy-3-formylbenzoic acid, m.p. $185-187^\circ$, reduced (Clemmensen) to 2:6-dimethoxy-*m*-toluic acid, m.p. $146-147^\circ$. The latter is obtained also from 2-hydroxy-6-methoxy-*m*-toluic acid, new m.p. $214-215^\circ$, and $Me_2SO_4-20\% KOH-COMe_2$. (II) and $2N-NaOH$ at 100° , or 2-methylresorcinol and aq. $KHCO_3$ ($100^\circ/4$ hr., then reflux for $\frac{1}{2}$ hr.) give 2:6-dihydroxy-*m*-toluic acid, m.p. $200-201^\circ$ (decomp.). (I) and $N-NaOH$ at room temp. for 45 hr. afford 2:4-dihydroxy-3-formylbenzoic acid, m.p. $193-194^\circ$ (decomp.), which with H_2O at $100-110^\circ$ (scaled tube) for 10 hr. gives γ -resorcyraldehyde (III), new m.p. $155-156^\circ$ (2:4-dinitrophenylhydrazones, m.p. $288-291^\circ$; semicarbazone, m.p. 245°), reduced (Clemmensen) to 2-methylresorcinol. (III) and $CH_3(CO_2Et)_2$ (piperidine) give Et 5-hydroxycoumarin-3-carboxylate, m.p. $229-230^\circ$. 3-Substitution in β -resorcylic acid or ester is not recorded previously. It is suggested that chelation between OH and CO_2Me in Me β -resorcyate leads to a fixation of the double linkings in the resorcinol nucleus, and a stabilisation of one of the Kekulé forms (cf. Baker *et al.*, A., 1937, II, 198). A. T. P.

Interaction between Grignard compounds and maleic acid derivatives. C. WEIZMANN and F. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 2647—2650).— Me_2 maleate (I) and $CH_2Ph \cdot MgCl$ give α -diphenyl- γ -benzylhexane- β -dione m.p. 136° , which gives no semicarbazone, but with $MgPhBr$ yields $\alpha\beta$ -triphenyl- δ -benzylhexan- β -ol- ϵ -one, m.p. 202° . $MgEtI$ and (I) give δ -ethyloctane- γ - δ -dione, b.p. $110^\circ/1$ mm. $MgBu^iBr$ and (I) give ζ -*n*-butyldodecane- ϵ - θ -dione (II), b.p. $136^\circ/0.05$ mm., and a little ϵ -*n*-butyl- Δ^4 -dodecen- ϵ -ol- θ -one (III), b.p. $115-120^\circ/0.1$ mm. With $MgPhBr$, (II) gives ϵ -diphenyl- ζ -*n*-butyl-*n*-dodecane- ϵ - θ -diol, m.p. $122-123^\circ$, and (?) dehydration products. $(CH_3CO)_2O$ with $CH_2Ph \cdot MgCl$, $MgBu^iBr$, and $MgEtBr$ gives γ -hydroxy- δ -phenyl- γ -benzyl- Δ^4 -pentenoic (p-

phenylphenacyl ester, m.p. 142—143°, γ -hydroxy- γ -n-butyl-n- Δ^8 -octenoic, b.p. 114°/0.05 mm. (p-phenylphenacyl ester, m.p. 79°), and γ -hydroxy- γ -ethyl-n- Δ^8 -hexenoic acid, b.p. 115°/0.6 mm. (p-phenylphenacyl ester, m.p. 77—78°), respectively, together with other products, which include α - ζ -diphenyl- β - ζ -dibenzyl- Δ^8 -hexatriene, m.p. 184°, b.p. 215—220°/1.5 mm. (from $\text{CH}_2\text{Ph}\cdot\text{MgCl}$), (III) (from MgBu^+Br), and (?) γ -ethylsorbic acid (p-phenylphenacyl ester, m.p. 138°) and α - ζ -diethyl-n-octan- ζ -ol- γ -one, b.p. 75°/1.5 mm. (from MgEtBr). γ -Butyrolactone and MgPhBr give α -diphenylbutane- α - δ -diol, m.p. 108°. The reaction mechanism is discussed. R. S. C.

Derivatives of β -p-anisyl- β -methylpyruvic [α -keto- β -p-anisylbutyric] acid. E. CATTELAINE (Compt. rend., 1938, 207, 998—1000).—The NaHSO_3 compound of α -p-anisylpropaldehyde (I) with cold aq. KCN affords α -hydroxy- β -p-anisylbutyronitrile, decomp. $\sim 50^\circ/15$ mm., converted by cold conc. HCl into α -hydroxy- β -p-anisylbutyramide (II), m.p. 123° (corresponding acid, m.p. 91—92°). (II) with KMnO_4 - COMe_2 affords α -keto- β -p-anisylbutyramide, m.p. 119—120° (semicarbazone, m.p. 239°), hydrolysed (warm dil. NaOH) to α -keto- β -p-anisylbutyric acid, m.p. 30° [semicarbazone, m.p. 207.5°, converted by warm dil. NaOH into 3:5-diketo-6- α -p-anisylethyl-2:3:4:5-tetrahydro-1:2:4-triazine, m.p. 220.5° (4-Me, m.p. 159—160°, 2:4-Me₂, m.p. 142.5°, 4-Et, m.p. 132°, 4-benzyl, m.p. 206°, and 2:4-dibenzyl, m.p. 160.5—161.5°, derivatives)]. J. L. D.

Synthesis of α -di-3:4-dimethoxyphenylbutan- β -one (veratryl homoveratryl ketone). R. CARROLL and P. E. SPOERRI (J. Amer. Chem. Soc., 1938, 60, 2656—2658).—

3:4-(OMe)₂C₆H₃·[CH₂]₂·COCl, b.p. 138—142°/0.5 mm., m.p. 40°, unstable, and CH₂N₂ in Et₂O give α -chloro- δ -3:4-dimethoxyphenylbutan- β -one, m.p. 53°, which, however, could not be caused to react with o-C₆H₄(OMe)₂. 3:4-(OMe)₂C₆H₃·CH₂·CN, 3:4-(OMe)₂C₆H₃·[CH₂]₂·CO₂Et, and NaOEt in EtOH give α -cyano- α -di-3:4-dimethoxyphenylbutan- β -one (I), m.p. 76°, which is difficult to hydrolyse but with conc. HCl-AcOH at 15—20° (4 days) gives α -carbonyl- α -di-3:4-dimethoxyphenylbutan- β -one, m.p. 123°, converted by hot, dil. HCl into α -di-3:4-dimethoxyphenylbutan- β -one, m.p. 76° [(NO₂)₂-derivative, m.p. 195°]. With hot, aq. H₂SO₄ (I) gives α -cyano-5:6:3':4'-tetramethoxy-1-benzylideneindane, m.p. 209°. R. S. C.

Friedel-Crafts reaction. IV. Action of acetyl chloride and acetic anhydride on resorcinol and its derivatives. Evidence for γ -substitution in the resorcinol nucleus. R. D. DESAI and M. EKHLAS (Proc. Indian Acad. Sci., 1938, 8, A, 194—201).—Resorcinol, AcCl, and AlCl₃ in PhNO₂ at room temp. yield 4:1:3- but no 2:1:3-C₆H₃Ac(OH)₂. Similarly 4:1:3-C₆H₃Et(OH)₂ yields 6:4:1:3-C₆H₂EtAc(OH)₂. 2:6-Dihydroxy-3-ethylacetophenone (I) (not formed in the above reaction), m.p. 135° [semicarbazone, m.p. 252°; Ac₂ derivative, m.p. 76° (semicarbazone, m.p. 267°)], is synthesised as follows: 5:2:4:1-C₆H₂Et(OH)₂·CO₂Me with Ac₂O and AlCl₃ in PhNO₂ yields Me 2:4-dihydroxy-3-acetyl-5-ethylbenzoate, m.p. 76°, hydrolysed (10% NaOH) to (I). 1:2:4-C₆H₃Et(OH)₂, CH₂Ac·CO₂Et, and 73% H₂SO₄

yield 7-hydroxy-4-methyl-6-ethylcoumarin [Me ether, m.p. 160°; carbethoxy-derivative (which failed to undergo the Fries transformation with AlCl₃ or ZnCl₂), m.p. 144°], the Ac derivative, m.p. 143°, of which with AlCl₃ at 140—150° yields 7-hydroxy-8-acetylcoumarin, m.p. 139° (semicarbazone, m.p. >290°). This is hydrolysed (2N-NaOH) to (I), with Ac₂O and NaOAc at 175—180° gives 3-acetyl-4:2'-dimethyl-6'-ethylcoumarin-7:8- γ -pyrone, m.p. 192°, and with Br in glacial AcOH in sunlight gives the 3-Br-compound, m.p. 180°, hydrolysed by Na₂CO₃ to 6-hydroxy-7-acetyl-3-methyl-5-ethylcoumarone (II), m.p. 66° (semicarbazone, m.p. >290°), together with the coumarilic acid, m.p. 204—206° (decomp.), decarboxylated to (II). 2:4:1-C₆H₃(OH)₂·CO₂Me does not condense with AcCl at room temp., but with Ac₂O and AlCl₃ in PhNO₂ yields 5:2:4:1- but no 3:2:4:1-C₆H₂Ac(OH)₂·CO₂Me. 4:1:3-C₆H₃Ac(OH)₂ under similar conditions yields both 2:4:1:3- and 4:6:1:3-C₆H₂Ac₂(OH)₂. Orcinol with AcCl and AlCl₃ in PhNO₂ yields orsacetophenone and a little 5-hydroxy-4:7-dimethylcoumarin [formed by way of 4:1:2:6-C₆H₂MeAc(OH)₂]. 2-Substitution in the m-C₆H₄(OH)₂ nucleus thus occurs in the last two cases only. A. LI.

Nuclear methylation of resacetophenone. 3-Methylresacetophenone and its derivatives.

S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1938, 8, A, 214—219).—1:2:4-C₆H₃Ac(OH)₂ with MeI-MeOH-KOH at 0° yields 2-hydroxy-4-methoxy-3-methyl-, m.p. 82—83°, demethylated to 2:4-dihydroxy-3-methyl-acetophenone, m.p. 156—157°, also synthesised from 2:1:3-C₆H₃Me(OH)₂, MeCN, ZnCl₂, and HCl.

2:4:1-C₆H₃(OH)₂·CO·CH₂·OMe with MeI-MeOH-KOH yields 2-hydroxy- ω :4-dimethoxy-3-methylacetophenone, m.p. 109°, which with NaOBz and Bz₂O at 200° gives 3:7-dimethoxy-8-methylflavone (I), m.p. 145—146°. ω -Methoxy-3-methylresacetophenone [from 2:1:3-C₆H₃Me(OH)₂, OMe·CH₂·CN, ZnCl₂, and HCl], m.p. 203—205°, with NaOBz and Bz₂O yields 7-hydroxy-3-methoxy-8-methylflavone, m.p. 252—253°, methylated (MeI-COMe₂-K₂CO₃) to (I). A. LI.

4-Acetyl-1-methylnaphthalene [and derivatives]. K. DZIEWOŃSKI and (MLLE.) M. MARUSIŃSKA (Bull. Acad. Polonaise, 1938, A, 316—323).—1-C₁₀H₇Me in PhNO₂, AcCl, and AlCl₃ at -3° to -1°, then at room temp. for 24 hr., give 4:1-C₁₀H₆AcMe (I), m.p. 41° (semicarbazone, m.p. 204—205°; phenylhydrazone, m.p. 141°) (cf. Haworth and Mavin, A., 1933, 57), the oxime, m.p. 125—126°, of which with dry HCl-Ac₂O-AcOH affords 1:4-C₁₀H₆Me·NHAc, new m.p. 171°, hydrolysed by boiling 10% HCl for 2 hr. to the amine, m.p. 51—52° (cf. Lesser, A., 1914, i, 33). (I) and 3% NaOCl give 1:4-C₁₀H₆Me·CO₂H, m.p. 175°. (I) and MgMeI-Et₂O yield 4-methyl-1-naphthylidimethylcarbinol (II), m.p. 85—86°, and 1-methyl-4-isopropenylnaphthalene, b.p. 140°/16 mm. (picrate, m.p. 89°). (I) and (II), with Zn-Hg-HCl-H₂O for 3 hr., give 1-methyl-4-ethyl-, b.p. 122°/40 mm. (picrate, m.p. 98—99°), and 1-methyl-4-isopropylnaphthalene, m.p. 196°, respectively. (I), NH₂Ph, and NH₂Ph·HCl at 170—175° for 2 hr. give 1:3:5-tri-(4'-methyl-1'-naphthyl)benzene, m.p. 185°; (I) and S

at 230—260° for 3 hr. afford 6 : 6'-dimethyl-4 : 5 : 4' : 5'-dibenzthioindigotin, m.p. >410°. A. T. P.

Ketone derivatives of 2 : 6-dimethylnaphthalene. K. DZIEWOŃSKI, K. STEC, and P. ZAGAJA (Bull. Acad. Polonaise, 1938, A, 324—330; cf. preceding abstract).—2 : 6-C₁₀H₆Me₂ and AcCl-PhNO₂-AlCl₃ at -4° give 2 : 6 : 1-C₁₀H₅Me₂Ac (I), m.p. 71° (semicarbazone, m.p. 193°) (cf. Clar *et al.*, A., 1929, 689), the *oxime*, m.p. 142—143°, of which with AcOH-Ac₂O-HCl affords 2 : 6 : 1-C₁₀H₅Me₂·NHAc, m.p. 205—206° (cf. A., 1922, i, 999), hydrolysed by 10% HCl (2 hr.) to 2 : 6 : 1-C₁₀H₅Me₂·NH₂ (II), m.p. 91°. (I) is oxidised (NaOCl) to 2 : 6 : 1-C₁₀H₅Me₂·CO₂H (III), m.p. 203—204°, and reduced (Clemmensen) to 2 : 6-dimethyl-1-ethylnaphthalene, b.p. 162°/23 mm. (picrate, m.p. 118°). EtCOCl similarly gives 1-propionyl-2 : 6-dimethylnaphthalene, m.p. 49°, b.p. 205—206°/23 mm. [picrate, m.p. 125°; semicarbazone, m.p. 188—189°; oxidised to (III)]; the *oxime*, m.p. 130°, affords 1-propionamido-2 : 6-dimethylnaphthalene, m.p. 199—200°, and thence (II). A. T. P.

Chalkones; synthesis of deoxybenzoin from chalkones. W. A. HUTCHINS, D. C. MOTWANI, K. D. MUDBHATKAL, and T. S. WHEELER (J.C.S., 1938, 1882—1885).—The possibility of conversion (cf. Baker and Robinson, A., 1932, 859) of COAr·CH·CHR' into COAr·CH₂R' is not independent of the nature of the substituent groups. Ph *p*-methoxystyryl ketone and NPh·NH₂·AcOH at 100° for 20 min. give 1 : 3-diphenyl-5-*p*-anisyl-4 : 5-dihydropyrazole, m.p. 125—126°. Ph, *p*-tolyl, 2 : 4 : 6-trimethoxyphenyl, and β-C₁₀H₇, m.p. 95—97°, *p*-methoxystyryl ketones, and 2 : 4-dimethoxyphenyl 3 : 4-methylenedioxy-styryl ketone, with 30% H₂O₂-EtOH-COMe₂-4*N*-NaOH at 40° afford Ph (I), *p*-tolyl (II), m.p. 109—110°, 2 : 4 : 6-trimethoxyphenyl (III), m.p. 118—120°, and β-C₁₀H₇ (IV), m.p. 131°, α,β-epoxy-β-*p*-anisylethyl ketone, and 2 : 4-dimethoxyphenyl α-β-epoxy-β-3 : 4-methylenedioxyphenylethyl ketone (V), m.p. 143°, respectively. *m*-Nitrophenyl *p*-methoxystyryl ketone and H₂O₂ do not react, neither is an oxide obtained from *m*-NO₂·C₆H₄·CO·CH₂Br and *p*-OMe·C₆H₄·CHO by the method of Widman (A., 1916, i, 406). (I) and (III), refluxed with aq. NaOH-EtOH for 4 hr., give Ph [also from (X) (below)] and 2 : 4 : 6-trimethoxyphenyl *p*-methoxybenzyl diketone, m.p. 144—145°, respectively. (IV) does not react similarly; (II) and (V) give unstable diketones, that from (II) with *o*-C₆H₄(NH₂)₂-EtOH giving 2-*p*-tolyl-3-*p*-methoxybenzylquinoxaline, m.p. 113—115°. (I), (II), and (V), boiled with 30% aq. NaOH for 4 hr., give phenyl- (VI) and *p*-tolyl-*p*-methoxybenzylglycollic acid (VII), m.p. 153°, and 2 : 4-dimethoxyphenyl-3 : 4-methylenedioxybenzylglycollic acid, m.p. 181°, respectively. The latter heated at > m.p. or with AcOH for 4 hr. gives 3 : 4-methylenedioxy-α-2' : 4'-dimethoxyphenylcinnamic acid, m.p. 176—177°. (VI) and (VII), with K₂Cr₂O₇ or K₂CrO₄ in aq. AcOH for 2 min., give Ph and *p*-tolyl *p*-methoxybenzyl ketone, m.p. 101—103°, respectively. (II) and (V), with N₂H₄·H₂O-EtOH for 5 min., give 4-hydroxy-5-*p*-anisyl-3-*p*-tolyl-4 : 5-dihydropyrazole (VIII), m.p. 168° (unstable NO-derivative), and 4-hydroxy-3-(2' : 4'-dimethoxyphenyl)-5-(3' : 4'-methylenedioxyphenyl)-4 : 5-

dihydropyrazole, m.p. 151°, respectively. (III) does not react similarly and (IV) gives an unstable derivative (IX). (I) affords 4-hydroxy-3-phenyl-5-*p*-anisyl-4 : 5-dihydropyrazole (Freudenberg *et al.*, A., 1925, i, 70) [ON(1)-Ac₂ derivative, m.p. 125—126°]. (VIII) and (IX), boiled with NaOEt-EtOH for 1½ hr., give 5-*p*-anisyl-3-*p*-tolyl-, m.p. 170°, and 3-β-naphthyl-, m.p. 232°, -pyrazoles, respectively. (I) or (V) and MeOH-H₂SO₄ at 40° for 3 hr., diluted slightly, then at 0° for some days, afford Ph α-hydroxy-β-methoxy-β-*p*-anisylethyl ketone (X), m.p. 87—89°, and 2 : 4-dimethoxyphenyl α-hydroxy-β-methoxy-β-3 : 4-methylenedioxyphenylethyl ketone, m.p. 200° (β-ethoxy-analogue, m.p. 172° from EtOH), respectively. (II) refluxed with AcOH for ½ hr. affords *p*-tolyl α-hydroxy-β-acetoxy-β-*p*-anisylethyl ketone, m.p. 103—105°, and (V) and HCO₂H give, similarly, 2 : 4-dimethoxyphenyl α-hydroxy-β-formoxy-β-3 : 4-methylenedioxyphenylethyl ketone, m.p. 212°. Ph *p*-methoxystyryl ketone, *p*-OMe·C₆H₄·CH₂·COPh, and EtOH-NaOEt give α-diketo-α,β-diphenyl-β-γ-di-*p*-anisylpentane, m.p. 165—166°. Similarly prepared are α-diketo-α-phenyl-β-γ-di-*p*-anisyl-α-, m.p. 146—147°, α-diketo-α,β-diphenyl-γ-*p*-anisyl-ε-, m.p. 152—153°, α-diketo-β-γ-di-*p*-anisyl-α-ε-di-, m.p. 150—151°, and α-diketo-γ-phenyl-ε-*o*-hydroxyphenyl-β-*p*-anisyl-α-, m.p. 167—168°, *p*-tolyl-pentane. 1 : 2-C₁₀H₆Ac·OMe and PhCHO in aq. EtOH-alkali give 2-methoxy-1-naphthyl styryl ketone, m.p. 140—142°, which with *p*-tolyl *p*-methoxybenzyl ketone gives α-diketo-γ-phenyl-β-*p*-anisyl-α-*p*-tolyl-ε-(2'-methoxy-1'-naphthyl)pentane, m.p. 156—157°. α-Diketo-α,βε-triphenyl-γ-*p*-anisylpentane and NH₂OH·HCl-EtOH at 140—145° for 5 hr. afford 2 : 3 : 6-triphenyl-4-*p*-anisylpyridine, m.p. 188—189°. cycloHexanone, *p*-OMe·C₆H₄·CH·COPh, and 50% NaOH-EtOH give 2-(β-benzoyl-α-*p*-anisylethyl)-cyclohexanone, m.p. 140—141°. Similarly prepared from *p*-tolyl and β-C₁₀H₇ *p*-methoxystyryl ketone and β-C₁₀H₇ styryl ketone (XI), m.p. 105—107°, are 2-(β-*p*-toluoyl-α-*p*-anisylethyl)-, m.p. 133—134°, 2-(β-naphthoyl-α-*p*-anisylethyl)-, m.p. 128—130°, and 2-(β-naphthoyl-α-phenylethyl)-, m.p. 155—156°, -cyclohexanone, respectively. (XI), β-C₁₀H₇ *p*-methoxystyryl and 1-hydroxy-2-naphthyl styryl ketones, respectively, refluxed with CH₂Ac·CO₂Et-NaOEt-EtOH for ½ hr., give *Et* 6-phenyl-4-β-naphthyl-, m.p. 174—175°, *Et* 6-*p*-anisyl-4-β-naphthyl-, m.p. 145—147°, and *Et* 6-phenyl-4-(1'-hydroxy-2'-naphthyl)-, m.p. 165—167°, -Δ³-cyclohexen-2-one-1-carboxylate.

A. T. P.

Influence of α-halogen substitution on the enolisation of ketones. E. P. KOHLER and H. M. SONNICHSEN (J. Amer. Chem. Soc., 1938, 60, 2650—2652).—The effect of α-halogen in increasing the enolisation of ketones is shown by (a) the solubility of α-bromo-ββ-diphenylpropionylmesitylene (I), m.p. 172—173°, in cold KOH-EtOH (it is only slightly sol. in EtOH) and (b) its conversion by KOH-MeOH-Me₂SO₄ into the *enol Me ether*, m.p. 115—116°, in 30% yield (traces are obtained by MeI). When kept in KOH-MeOH, (I) gives 2 : 4 : 6-C₆H₂Me₃·CO·CH·CPh₂ (II), 80—90% of (I) is obtained from 2 : 4 : 6-C₆H₂Me₃·CO·CH·CPh₂ by MgPhBr, followed by Br at < -5°. 2 : 4 : 6-C₆H₂Me₃·CO·CH₂·CPh₂ or (I) with Br in aq. alkali

gives α -dibromo- β - β -diphenylpropionylmesitylene, m.p. 135—136°, unstable when heated, converted slowly by aq. KOH or more rapidly by KOH-MeOH into (II). $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{COPh}$ is sol. in MeOH-KOH, although less so than (I), but is thereby converted into a substance, m.p. 230—240°. R. S. C.

Reaction of diazomethanes with Grignard reagents. G. H. COLEMAN, H. GILMAN, C. E. ADAMS, and P. E. PRATT (J. Org. Chem., 1938, 3, 99—107).— MgPhBr adds to the terminal N of CPh_2N_2 (modified prep.), giving, after hydrolysis, $\text{CPh}_2\text{N}\cdot\text{N}\cdot\text{NHPh}$. If $\text{NPh}_2\cdot\text{COCl}$ is added before hydrolysis, the intermediate $\text{CPh}_2\text{N}\cdot\text{N}\cdot\text{NPh}\cdot\text{MgBr}$ reacts therewith to give *benzophenone- β - δ -triphenylsemicarbazone*, $\text{CPh}_2\text{N}\cdot\text{N}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$, m.p. 160—161°, obtained also by treating $\text{CPh}_2\text{N}\cdot\text{N}\cdot\text{NHPh}$ first with MgPhBr or NaNH_2 and then with $\text{NPh}_2\cdot\text{COCl}$, and hydrolysed by hot 20% HCl to COPh_2 and $\text{NH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{NPh}_2$. Similarly with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$, CPh_2N_2 gives $\text{CPh}_2\text{N}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ or, if treated with $\text{NPh}_2\cdot\text{COCl}$, *benzophenone- δ - δ -diphenyl- β -benzylsemicarbazone*, m.p. 137—139°, obtained also from $\text{CPh}_2\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$ by MgPhBr , followed by CH_2PhCl , and hydrolysed to COPh_2 and δ - δ -diphenyl- β -benzylsemicarbazide, $\text{NH}_2\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{CO}\cdot\text{NPh}_2$, m.p. 109—110°. With MgMeI CPh_2N_2 gives $\text{CPh}_2\text{N}\cdot\text{N}\cdot\text{NHMe}$, hydrolysed to $\text{NH}_2\cdot\text{NHMe}$. With a slight excess of MgPhBr CH_2N_2 gives indefinite products, but with a large excess reacts thus: $\text{CH}_2\text{N}_2 + \text{MgPhBr} \rightarrow \text{CH}_2\text{N}\cdot\text{N}\cdot\text{NPh}\cdot\text{MgBr} \rightarrow \text{CH}_2\text{Ph}\cdot\text{N}(\text{MgBr})\cdot\text{NPh}\cdot\text{MgBr} \rightarrow \text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NHPh}$ (I) (identified by oxidation by H_2O_2 to $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$). In the reaction of CH_2N_2 with $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ or MgBu^nBr reduction occurs, the products being α -benzyl- β -methylhydrazine (*hydrochloride*, m.p. 139—140°; reduced by Na-Hg to NH_2Me and $\text{NH}_2\cdot\text{CH}_2\text{Ph}$) and α -methyl- β -*n*-butylhydrazine (*hydrochloride*, m.p. 114—115°), respectively. CH_2N_2 with MgEtI , MgMeI , and MgMeBr gives N_2 and indefinite products. R. S. C.

Degree of association of metal diaryl ketyls. L. ANSCHÜTZ and A. UNGAR (Annalen, 1938, 536, 285—297).—The effect of the addition of K on the b.p. of solutions of Ph diphenyl ketone (I) in Et_2O , C_6H_6 , and dioxan (II), of COPh_2 in C_6H_6 , and of *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{COPh}$ in C_6H_6 and (II) has been studied. Solutions sufficiently conc. for the determination of mol. wt. are invariably supersaturated. In 36 successful experiments the results obtained agree satisfactorily with those required for the monomeric compound, the extreme deviations being -13% and +6%. Under the most favourable circumstances solutions of (I) in Et_2O and (II) give about 28% and 68%, respectively, of the theoretical amounts of metal ketyl. The metal diaryl ketyls have very little tendency towards association (cf. Doescher *et al.*, A., 1934, 1158). H. W.

Structure and absorption [spectra] of benzoylbenzoic acid and its derivatives. C. K. LIN (Compt. rend., 1938, 207, 733—735; cf. A., 1917, i, 339; 1922, i, 833).—Comparison of the ultra-violet absorption spectra of *o*-benzoyl-*p*-methoxybenzoic acid (I), *o*- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$ (II), their Me esters, and Na salts with those of *p*-methoxyphenyl- and phenyl-

phthalide, respectively, indicates that (I) and (II) exist in solution (Et_2O , EtOH) in the ketonic forms.

J. L. D.

Catalytic properties of the phthalocyanines. III. A. H. COOK (J.C.S., 1938, 1774—1780; cf. A., 1939, I, 34).—The oxidation of tetra- and Δ^2 -octa-(I)-hydronaphthalene, α -pinene, cyclohexene, Δ^1 -methylcyclohexene, CH_2Ph_2 , and cholesteryl acetate by O_2 in presence of Fe phthalocyanine, yielding products containing CO and only rarely OH adjacent to the double linking, has been studied. Of 38 other metal phthalocyanines and related pigments, all were inactive except Cr and Co phthalocyanines, which were feebly active. Evidence for the formation of an intermediate peroxide of the compound being oxidised is discussed. The catalyst functions partly by promoting the formation of the peroxide and partly by accelerating its further rearrangement to a ketone. The product of oxidation of (I) is 1-*keto*- Δ^2 -octahydronaphthalene, b.p. 114°/5 mm. (*semicarbazone*, m.p. 203—204°). 3-Methyl- Δ^2 -cyclohexenone-2:4-dinitrophenylhydrazone has m.p. 150°.

E. S. H.

Condensation of acenaphthenequinone with xlenols and thymol. I. MATEI and E. BOGDAN (Ber., 1938, 71, [B], 2292—2295; cf. A., 1935, 86).—Addition of a few drops of conc. H_2SO_4 to acenaphthenequinone and 3:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ in boiling AcOH affords *anhydro-8-keto-7:7-di-2'-hydroxy-4':5'-dimethylphenylacenaphthene* (+1AcOH), m.p. 301°. Under similar conditions 2:5- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ yields *8-keto-7:7-di-4'-hydroxy-2':5'-dimethylphenylacenaphthene* (+1EtOH), m.p. 167—171° and, after re-solidification, m.p. 246—247° (also +1Et₂O); the diacetate (+1EtOH) has m.p. 198°. Thymol yields *8-keto-7:7-di-4'-hydroxy-2'-methyl-5'-isopropylacenaphthene*, m.p. 197° (dibenzoate, m.p. 107°). 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$ gives *anhydro-8-keto-7:7-di-2'-hydroxy-3':5'-dimethylphenylacenaphthene* (I) (+0.5PhNO₂), m.p. >350°, and *anhydro-7:8-di-2'-hydroxy-3':5'-dimethylphenylacenaphthene-7:8-diol* (+COMe₂), m.p. 281—282°, transformed by conc. H_2SO_4 in AcOH into (I). H. W.

Hydroxy- and methoxy-phenylanthrones. I. II. F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1938, 60, 2638—2641, 2642—2644).—I. Addition of *o*- $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ or *o*- $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ to *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{MgI}$ in C_6H_6 - Et_2O gives an oily carbinol, converted by HCl in AcOH or EtOH into 9:9-di-*p*-anisyl-9:10-dihydroanthracene, m.p. 166—167° (oxidised to the known anthrone). *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ (I) and *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{MgI}$ give 4':4''-dimethoxy-2-*p*-methoxybenzyltriphenylcarbinol, m.p. 147—148°, converted by HCl into 2-methoxy-9:9-di-*p*-anisyl-9:10-dihydroanthracene, m.p. 167—168°, oxidised to the known methoxy-anthrone, which with AlCl_3 in hot C_6H_6 gives 2-hydroxy-9:9-di-*p*-hydroxyphenyl-10-anthrone, m.p. 312—314° (decomp.) [(*m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}$)₃ derivative, m.p. 174—176°]. *Et o-o'*-methoxybenzylbenzoate, b.p. 268—270°/14 mm., gives similarly 4':4''-dimethoxy-2-*o*-methoxybenzyltriphenylcarbinol, m.p. 139—140°, and thence, by way of the 9:10- H_2 -compound, 4-methoxy-9:9-di-*p*-anisyl-10-anthrone,

m.p. 248—250°, and 4-hydroxy-9:9-di-*p*-hydroxyphenyl-10-anthrone, m.p. 254—256° (decomp.) [(m-C₆H₄Br·CO)₃ derivative, m.p. 163—165°]. With *o*-OMe·C₆H₄·MgI (I) gives 2':2'-dimethoxy-2-*p*-methoxybenzyltriphenylcarbinol, m.p. 129—130°, and thence 2-methoxy-9:9-di-*o*-anisyl-9:10-dihydroanthracene, m.p. 154—155°. 3-Methoxy-10-anthrone and Br·CS₂ at -5° give the 9:9-Br₂-derivative, m.p. 175—177°, which could not be condensed with PhOMe, but with Hg in C₆H₆ gives 2:2'- or 2:7'-dimethoxydianthraquinone, $\left[\text{CO} < \begin{array}{c} \text{C}_6\text{H}_3(\text{OMe}) \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \right]_2$, m.p. 254—256° (decomp.).

II. *o*-CO₂H·C₆H₄·CH(C₆H₄·OR-*p*)₂ (R = H or Ac) with ZnCl₂·Ac₂O at 100° gives 3:10-diacetoxy-9-*p*-acetoxyphenylanthracene, m.p. 188—189°, oxidised by Na₂Cr₂O₇ in hot AcOH to 9-hydroxy-3-acetoxy-9-*p*-acetoxyphenyl-10-anthrone (II), m.p. 186—187°, which, when rapidly hydrolysed, gives 3:9-dihydroxy-9-*p*-hydroxyphenyl-10-anthrone (III), m.p. 127—128° (3:4'-Me₂ ether, m.p. 155—156°). With mineral acids or when heated, (III) loses H₂O and gives a fuchsone. With HCl·AcCl·C₆H₆, (II) gives 9-chloro-3-acetoxy-9-*p*-acetoxyphenyl-10-anthrone, m.p. 128—129°, which with Ag gives the free radical (intense red) and thence the 9:9'-peroxide, m.p. 195—200° (decomp.). 2:5-Di-*p*-anisyl-3:4-benzofuran and Na-Hg in abs. EtOH give the 2:5-H₂-derivative, m.p. 115—116°, which with Na₂Cr₂O₇ gives *o*-C₆H₄(CO·C₆H₄·OMe-*p*)₂; with Na-Hg·EtOH this yields *o*-di-(α -hydroxy-*p*-methoxybenzyl)benzene, m.p. 139—140°, converted by ZnCl₂·Ac₂O·AcOH into 2-methoxy-9-*p*-anisylantracene, m.p. 177—179° (lit., 175—176°), and thence 9-hydroxy-2-methoxy-9-*p*-anisyl-, m.p. 202—203° (lit., 199—201°), and 2-methoxy-9:9-di-*p*-anisyl-10-anthrone.

R. S. C.

Deviations in the Claisen condensation. (SIGNA.) M. FRERI (Gazzetta, 1938, 68, 612—618).—The product of this condensation depends on the alkoxide used as condensing agent. Thus COMe₂ and Et₂C₂O₄, which in presence of NaOEt yield the Et ester of acetylpyruvic acid (A., 1912, i, 936), in presence of NaOMe form the Me ester, m.p. 63° (in each case the Na salt is first obtained, and is decomposed by dil. H₂SO₄ or by AcOH). Similarly COPhMe and either Et₂C₂O₄ or PrⁿC₂O₄ with NaOMe give Me, m.p. 60°, with NaOEt give Et, and with NaOPrⁿ give Prⁿ benzoylpyruvate, m.p. 68°. Me₂C₂O₄ under similar conditions does not react. The mechanism of the reaction is discussed. E. W. W.

New derivatives of mesobenzanthrone. W. H. D. BOYES, J. L. GRIEVE, and H. G. RULE (J.C.S., 1938, 1833—1841; cf. A., 1935, 859).—1:2-C₁₀H₆Br·CN (prep. from 1:2-C₁₀H₆Br·NH₂) is hydrolysed (H₂SO₄·AcOH·H₂O) to 1:2-C₁₀H₆Br·CO₂H, new m.p. 191°, the Me ester, m.p. 60°, of which with *o*-C₆H₄I·CO₂Me + Cu-bronze at 175—180° gives Me diphenate and (after heating with H₂SO₄) fluorenonecarboxylic acid (extracted with PhCl) and benzanthr-7-one-1-carboxylic acid (I), m.p. 285° (3% yield). (I) and *o*-C₆H₄(CO)₂O·P₂O₅ at 200° for 2 hr. give 1:11-ketobenzanthrone-7 (II); quinoline + Cu bronze afford mesobenzanthrone, whilst oxidation (CrO₃, dil. H₂SO₄) gives anthraquinone-1-carboxylic

acid. Br converts (I) in boiling dil. H₂SO₄ into the 3-Br-derivative, m.p. 319—320°, converted by *o*-C₆H₄(CO)₂O·P₂O₅ at 200° into 3-bromo-1:11-ketobenzanthrone. (I) and boiling conc. HNO₃ give a nitrated (?) lactone, m.p. 256—257°, of 11-hydroxybenzanthr-7-one-1-carboxylic acid. Benzanthrone-11-carboxylic acid (III) and Cl₂ in boiling dil. H₂SO₄ for 4 hr. give the 3-Cl-derivative, m.p. 317—318°, decarboxylated (quinoline+Cu) to 3-chlorobenzanthrone. Br similarly gives the 3-Br-derivative of (III) (cf. A., 1937, II, 424), but Br in boiling PhNO₂ for 3 hr. affords the lactone (IV) of 1-hydroxybenzanthrone-11-carboxylic acid. (III) and HNO₃ (d 1.42)·H₂SO₄ at 0° for 15 min. give the 3-NO₂-derivative (V), m.p. 310° (decomp.), whereas boiling HNO₃ affords the lactone, m.p. 317—318° (decomp.), of 3-nitro-11-hydroxybenzanthrone-11-carboxylic acid, also obtained similarly from (IV), or from (V) and CrO₃. (III) and excess of conc. HNO₃ in boiling AcOH yield only (IV). NaN₃ and (II) in H₂SO₄ + CHCl₃ at 45—50° give 11-aminobenzanthrone, m.p. 215—217° (HCO, m.p. 268—271°, and Ac, m.p. 278—279°, derivatives), converted by KOH at 220° for ½ hr. into (?) diaminodibenzanthrone. Benzanthrone-11-carboxylamide (VI), from the acid chloride and conc. aq. NH₃, sinters at 300—310°, softens at 320°, melts at 325—327°, and resolidifies at 327—330°; it is best hydrolysed [to (III) and ~25% of (IV)] by HNO₂. H₂SO₄·H₂O·CrO₃ and (VI) give (IV), but with PhNO₂·Br the lactam, m.p. >360°, of 1-aminobenzanthrone-11-carboxylic acid results. (II) and Cl₂ in AcOH (100°) for 10 min., or better in dil. H₂SO₄ at b.p. for 3 hr., give the 3-Cl-derivative, m.p. 335—336°, sinters at 245°, obtained also by cyclising 3-chlorobenzanthrone-11-carboxylic acid. Further chlorination in AcOH for 1 hr. gives a mixture, m.p. 334—339°, of isomeric Cl₂-derivatives. (II) and dil. H₂SO₄·Br (not in AcOH or PhNO₂) for 4 hr. give the 3-Br-derivative; with excess of Br at 50—60° for 2 hr. the 3:9-Br₂-compound results. (II)·H₂SO₄·HNO₃ (d 1.42) for ½ hr. give the 3-NO₂-derivative, m.p. 284—285°, but excess of boiling HNO₃ gives an inseparable mixture. Benzanthrone-1:11-ketoxime (VII), m.p. 314°, is partly hydrolysed by boiling PhNO₂ to a 1:1 mol. compound, m.p. 322°, of (II) and PhNO₂, the latter being lost at 220° in 2 hr. (VII) and PhOMe·PCl₅ at 75° for 5 hr. afford the lactam (VIII), m.p. >360°, of 11-aminobenzanthrone-1-carboxylic acid (or the 1:11-compound), best prepared from (II) and NaN₃ in H₂SO₄. (VIII) fused with KOH at 280° for 1 hr. gives a crude dilactam of dibenzanthrone type (vat dye). 3:8:1-NO₂·C₁₀H₅Br·CO₂Me and *o*-C₆H₄I·CO₂Me + Cu bronze at 160° for 1 hr., then 180° for 3 hr., give Me 3-nitro-8-(*o*-carboxymethoxyphenyl)-1-naphthoate, m.p. 143°, converted by H₂SO₄ at 80° for ½ hr. or 100° for 1 hr. into 5-nitrobenzanthrone-11-carboxylic acid (IX), m.p. 309° (decomp.), or its anhydride, respectively. (IX) is converted by boiling quinoline and Cu-bronze into 5-nitrobenzanthrone, m.p. 287°, and by P₂O₅ in *o*-C₆H₄(CO)₂O into 5-nitro-1:11-ketobenzanthrone, m.p. 319—320° (13% yield).

A. T. P.

Derivatives of croconic acid. R. MALACHOWSKI and S. PREBENDOWSKI (Ber., 1938, 71, [B], 2241—

2247).—Ag₂ croconate (I) and MeI in abs. Et₂O at room temp. yield Me₂ croconate (II) [3 : 4 : 5-triketo-1 : 2-dimethoxy-Δ¹-cyclopentene], m.p. 114—115°, b.p. 250°/740 mm. (incipient decomp.), which is rapidly hydrolysed when exposed to air. Et₂ croconate, b.p. 174—175°/3 mm., m.p. 57.5—58.5°, is obtained similarly. *o*-C₆H₄(NH₂)₂ and (II) in MeOH give the quinoxaline derivative, C₆H₄ $\begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CO} \\ \text{N} \cdot \text{C} \cdot \text{C}(\text{OMe}) \end{smallmatrix}$ >C·OMe, m.p. 166°, transformed by an excess of KOH into the salt, C₁₂H₇O₃N₂K, whence the acid, C₁₂H₅O₃N₂, m.p. >340°. (I) is transformed by HCl-EtOH at room temp. into croconic acid β-Et₂ acetal [1 : 2-dihydroxy-3 : 5-diketo-4 : 4-diethoxy-Δ¹-cyclopentene] (III), also obtained from croconic acid (IV). It has no definite m.p. When distilled with C₆H₆ it gives Et H croconate, decomp. >150°. With CH₂N₂-Et₂O (III) yields Me₂ croconate β-Et₂ acetal, b.p. 163—165°/11 mm., which does not condense with *o*-C₆H₄(NH₂)₂ and is hydrolysed slowly by cold but immediately by hot acids or alkalis to the free acid. It condenses with (CH₂NH₂)₂ to a mixture of the compound, (CO·CH(OMe) $\begin{smallmatrix} \text{CO} \\ \text{C} \cdot \text{N} \cdot \text{CH}_2 \end{smallmatrix}$), m.p. 123° [which does not give a colour with FeCl₃ and is converted by warm dil. HCl into (IV)], and the dihydropyrazine, CH₂N·N·C·C(OMe) $\begin{smallmatrix} \text{CO} \\ \text{C} \cdot \text{CH}(\text{OMe}) \end{smallmatrix}$ >CO, m.p. 124—125°, which is neutral, does not give a colour with FeCl₃, is unchanged by short warming with H₂O or dil. NaOH but readily transformed by dil. HCl into the diketone, CH₂N·N·C·CO $\begin{smallmatrix} \text{CO} \\ \text{C} \cdot \text{CH}(\text{OH}) \end{smallmatrix}$ >CO, decomp. >300°, which with CH₂(NH₂)₂ gives the bisdihydropyrazine, C₉H₁₀ON₄, m.p. 208° (decomp.), also obtained from (II) and (CH₂NH₂)₂ in EtOH. H. W.

Unsaturated ketones of the androstane and pregnane series.—See B., 1938, 1502.

Ketones of the cyclopentanopolyhydrophenanthrene series.—See B., 1938, 1502.

Relatively inert oxygen atom of digoxigenin, sarmentogenin, and the steroid compounds of the adrenal cortex. H. L. MASON and W. M. HOEHN (J. Amer. Chem. Soc., 1938, 60, 2824).—The diketone-eholanic and -cholenic acid of the authors (A., 1938, II, 329, 497) and of Steiger and Reichstein (*ibid.*, 329) are shown by direct comparison to be identical, but the (OH)₂-acids are different (epimeric at C₍₁₂₎). The indifferent O of the steroids named is thus at C₍₁₁₎. R. S. C.

Syntheses in the hydroaromatic series. IV. (A) Condensation of 3-methyl-Δ³-cyclopentene-1 : 2-dione with 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene. (B) Preparation and diene syntheses of 3-hydroxy-2 : 6-dimethyl-*p*-benzoquinone. E. DANE and J. SCHMITT (Annalen, 1938, 536, 196—203).—(A) 6-Methoxy-1-acetylenyl-3 : 4-dihydronaphthalene is hydrogenated (Pd-C in dioxan) to the 1-vinyl derivative (I), which is condensed with 3-methyl-Δ³-cyclopentene-1 : 2-dione at 120° to a compound, C₁₉H₂₀O₃, m.p. 170° (red) after softening.

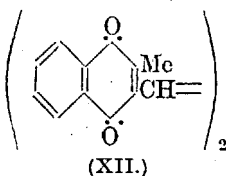
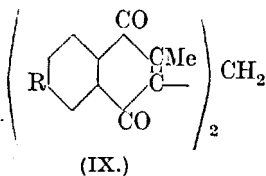
(B) 3 : 5-Dimethyl-Δ³-cyclohexenone (II) is oxidised by SeO₂ in AcOH at 100° to 3-hydroxy-2 : 6-dimethyl-

p-benzoquinone (III), m.p. 103°, and an additive compound (1 : 1), m.p. 41°, of 1 : 3 : 5-C₆H₃Me₂·OH and (II). Butadiene and (III) at 110° give almost quantitatively 3-hydroxy-2 : 9-dimethyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone, m.p. 120°, which gives a very marked reaction with FeCl₃ and is reduced (Pd-C in cyclohexane) to a H₄-derivative, m.p. 117.5°. (I) and (III) yield the chrysene derivative, C₂₂H₂₂O₄, m.p. 167.5°. H. W.

Syntheses and reactions of substituted α-naphthaquinones. E. BERGMANN and F. BERGMANN (J. Org. Chem., 1938, 3, 125—136).—Toluquinone and (CH₃·CMe)₂ at 110° give 2 : 6 : 7-trimethyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone (I), m.p. 93—94°, rearranged by a drop of HBr in AcOH to 1 : 4-dihydroxy-2 : 6 : 7-trimethyl-5 : 8-dihydronaphthalene (II), m.p. 224°; however, at 150—170° rearrangement occurs, giving (II) and, sometimes, by oxidation, 2 : 6 : 7-trimethyl-1 : 4-naphthaquinone (III), m.p. 110°. FeCl₃-EtOH oxidises (II) to 2 : 6 : 7-trimethyl-5 : 8-dihydro-1 : 4-naphthaquinone (IV), m.p. 129°. Se converts (I) or (IV) into (III). Phenyl-*p*-benzoquinone (V) and (CH₃·CMe)₂ at 100° give 2-phenyl-6 : 7-dimethyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone (VI), m.p. 113—114°, rearranged by HBr-AcOH into 1 : 4-dihydroxy-2-phenyl-6 : 7-dimethyl-5 : 8-dihydronaphthalene (VII), m.p. 137°, which with FeCl₃-EtOH gives 2-phenyl-6 : 7-dimethyl-5 : 8-dihydro-1 : 4-naphthaquinone (VIII), m.p. 119°. With Se at 280—300° (VI) gives 1 : 4-dihydroxy-2-phenyl-6 : 7-dimethylnaphthalene, m.p. 197—198°, oxidised by FeCl₃ to 2-phenyl-6 : 7-dimethyl-1 : 4-naphthaquinone, m.p. 127° [which is obtained also from (VIII) by Se or in traces by the original diene reaction at 150—200°], and [as is (VI)] by air in KOH-EtOH to 3-hydroxy-2-phenyl-6 : 7-dimethyl-1 : 4-naphthaquinone, m.p. 158° (Me ether, m.p. 186°). cyclopentadiene and (V) in hot C₆H₆ give the normal adduct, C₁₇H₁₄O₂, m.p. 79—80°.

CH₂N₂ usually adds to 1 : 4-naphthaquinones in the 2 : 3-positions, giving the pyrazoline, which decomposes, when heated, into N₂ and a methylated quinone. 2-Bromo-1 : 4-naphthaquinone and CH₂N₂ give a product, m.p. 272—280° (decomp.), which with conc. aq. NH₃ loses HBr and yields 3 : 4-phthalalpyrazole, m.p. 345°. CH₂N₂ and (VI) give the pyrazole derivative, C₁₉H₂₀O₂N₂, b.p. 170°/0.3 mm. CH₂N₂ adds to (I), giving 3 : 4' : 5'-trimethyl-3 : 4-Δ^{4'}-tetrahydrophthalyl-Δ¹-2-pyrazoline, CMe·CH₂·CH·CO·CMe·N $\begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix}$ >N, m.p. 146° (decomp.), decomposed in light petroleum at 130° into 2 : 3 : 6 : 7-tetramethyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone, a resin, which is isomerised by HBr-AcOH to 1 : 4-dihydroxy-2 : 3 : 6 : 7-tetramethyl-5 : 8-dihydronaphthalene, m.p. 232°, which with FeCl₃ yields 2 : 3 : 6 : 7-tetramethyl-5 : 8-dihydro-1 : 4-naphthaquinone, m.p. 155—156°. CH₂N₂ and (III) in MeOH give a crude product, m.p. 175°, which, when recrystallised, is oxidised to 2 : 3 : 6 : 7-tetramethyl-1 : 4-naphthaquinone, m.p. 167—168°. 2-Methylnaphthaquinone and CH₂N₂ in Et₂O at 0° give the normal adduct, C₁₂H₁₀O₂N₂, m.p. 114°, a product (IX) (R = H), m.p. 242°, and an oil, which, when distilled, gives 2 : 3-dimethylnaphthaquinone (X).

2 : 6-Dimethyl-1 : 4-naphthaquinone (XI) and CH_2N_2 at 0° give the *hydroquinone*, $\text{C}_{25}\text{H}_{22}\text{O}_4$, m.p. 293° [considered by Fieser *et al.* (A., 1935, 217) to be (IX) ($\text{R} = \text{Me}$) and given m.p. 300° ; oxidised by FeCl_3 to the *diquinone* (IX) ($\text{R} = \text{Me}$), m.p. 249°], and an oil, which, when distilled, gives 2 : 3 : 6-trimethyl-1 : 4-naphthaquinone, m.p. 100° ; sometimes a product, m.p. 228.5° , was also formed in small amount. With Zn dust and AcOH in EtOH (XI) gives 1 : 4-dihydroxy-2 : 6-dimethylnaphthalene, m.p. $187-188^\circ$ (Me_2 ether, b.p. $129^\circ/0.5$ mm., m.p. $75-76^\circ$). When kept in dil. KOH-MeOH , (X) gives the *diquinone* (XII), m.p. $227-228^\circ$, oxidised by FeCl_3 to a substance, $\text{C}_{24}\text{H}_{16}\text{O}_5$, m.p. 184° . CHPh_2Na in Et_2O causes enolisation of



(X) to 1-hydroxy-4-keto-2-methyl-3-methylene-3 : 4-dihydronaphthalene (XIII); some CHPh_2Na adds to (XIII), giving 2- $\beta\beta$ -diphenylethyl-3-methyl-1 : 4-naphthaquinone, m.p. 167° ; a second mol. of (X) also adds to (XIII) and, if air is passed through the mother-liquors, the *diquinone* [(XII) with $\cdot\text{CH}_2\cdot$ for $\cdot\text{CH}=\cdot$], m.p. $261-262^\circ$, or sometimes (XII) is obtained.

R. S. C.

Condensation of phthalic anhydride with *p*-dichlorobenzene. I. M. KOGAN and T. N. GANINA (Prom. Org. Chim., 1936, 1, 87-91).— $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, $\text{p-C}_6\text{H}_4\text{Cl}_2$ (5 mols.), and AlCl_3 (4 mols.) at $110^\circ/6$ hr. give *o*-2 : 5-dichlorobenzoylbenzoic acid (59.3%), converted by 5% oleum (7 parts) at $150^\circ/4$ hr. into 1 : 4-dichloroanthraquinone (83.5%).

CH. ABS. (c)

Intra-complex coloured compounds. Constants of alizarin and alizarates.—See A., 1939, I, 25.

Friedel-Crafts reaction. III. Condensation of acylarylamides and aromatic and heterocyclic amines with phthalic anhydride. P. KRÄNZLEIN (Ber., 1938, 71, [B], 2328-2335; cf. A., 1937, II, 432, 460).—Replacement of AlCl_3 in $\text{C}_2\text{H}_5\text{Cl}$ by a molten mixture of NaCl and AlCl_3 frequently permits the conversion of amines directly into substituted anthraquinones without preliminary acylation or isolation of any intermediate. Successive additions of 1 : 3 : 4- $\text{NHAc-C}_6\text{H}_3\text{Me-OH}$ and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ to $\text{AlCl}_3\text{-NaCl}$ (3 : 1) at $115-120^\circ$ give a 64% yield of *o*-2-acetamido-5-hydroxy-4-methylbenzoylbenzoic acid, m.p. 263° , converted by conc. H_2SO_4 at 100° into 1-amino-4-hydroxy-3-methylanthraquinone, m.p. 237° . Similarly, $\text{p-C}_6\text{H}_4\text{Ph-NHAc}$ and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ yield *o*-4-*p*-acetamidophenylbenzoylbenzoic acid, m.p. 256° , converted by conc. H_2SO_4 at 110° into 2-*p*-aminophenylantraquinone, m.p. 221° , also obtained directly (45% yield) from $\text{p-C}_6\text{H}_4\text{Ph-NH}_2$ and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ and $\text{AlCl}_3\text{-NaCl}$ at 120° and subsequently at $150-155^\circ$. 3 : 1 : 4- $\text{C}_6\text{H}_3\text{MePh-NHAc}$ and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ give (84% yield) *o*-*p*'-4'-acetamido-3'-methylphenylbenzoylbenzoic

acid, m.p. 238° , transformed by conc. H_2SO_4 at 110° (yield 92%) into 2-4'-amino-3'-methylphenylantraquinone, m.p. 199° , also obtained directly from 3 : 1 : 4- $\text{C}_6\text{H}_3\text{MePh-NH}_2$. 2-Aminocarbazole and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ with $\text{AlCl}_3\text{-NaCl}$ at $110-115^\circ$ and then at 150° afford 2-aminophthalylcarbazole, m.p. 355° , in 65-70% yield. The following compounds are prepared analogously: 3-amino-*N*-ethylphthalylcarbazole, m.p. 296° ; 2-aminophthalyl-diphenylene oxide, m.p. $>300^\circ$ (slow decomp.) after softening at 295° (Bz derivative, m.p. 338°); 3-aminophthalylphenanthrene, m.p. 291° ; 2-aminophthalylfluorene, m.p. 293° ; 2-aminophthalylchrysene, m.p. 325° after softening at 320° ; 4-aminophthalylfluoranthene, m.p. $>350^\circ$; 3-aminophthalylpyrene, m.p. $>350^\circ$.

H. W.

Dyes derived from chrysoquinone. K. M. P. SINGH and S. DUTT (Proc. Indian Acad. Sci., 1938, 8, A, 187-193).—Chrysoquinone (I) (bisphenylhydrazone, m.p. $228-229^\circ$) yields, with conc. HNO_3 in the cold, *nitro*-, m.p. $256-257^\circ$, and at 100° , *dinitro*-, m.p. 235° , and with fuming HNO_3 (d 1.5) at 100° , *tetranitro-chrysoquinone*, m.p. $>300^\circ$. None of these could be reduced to the amine. (I) with Br at 110° yields in PhNO_2 , a Br_1 -compound, m.p. 246° , and in glacial AcOH , an *isomeride*, m.p. 218° , and with excess of Br in a sealed tube, *pentabromochrysoquinone*, m.p. $>300^\circ$. These with NH_2Ph and Cu-bronze yield, respectively *anilino*-, m.p. $210-212^\circ$ and $153-155^\circ$, and *bromotetra-anilino-chrysoquinone*, m.p. $291-293^\circ$. With $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, 1 : 2- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$, $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and 2 : 3-diaminophenazine in glacial AcOH , (I) yields respectively *chryso-phenazine*, m.p. $207-208^\circ$ (PhNO_2), 199° (AcOH), 1 : 2-naphthazine, m.p. 238° , *phenoxazine*, m.p. 236° , and 2 : 3-diaminophenazine, m.p. $>300^\circ$. The following were obtained from (I) and NH_2Ar (excess) in hot glacial AcOH : *chrysoquinonediphenyl*-, m.p. $228-229^\circ$, *o*-, m.p. $>300^\circ$, and *m-tolyl*-, m.p. $163-165^\circ$, *o-anisyl*-, m.p. $160-163^\circ$, *o*-, m.p. $188-190^\circ$, and *p-phenetyl*-, m.p. $205-207^\circ$, α -, m.p. $198-200^\circ$, and β -naphthyl-imine, m.p. 203° . The dyeing properties of these compounds are described.

A. LI.

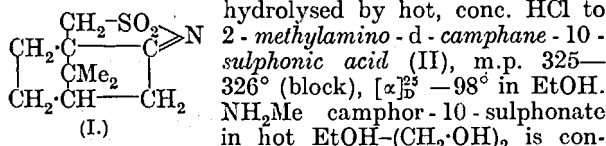
Action of hydroxylamine on camphor- and dithiocamphor-imide. A. MANNESIER-MAMELI (Congr. int. Quim. pura apl., 9, IV, 588-593; Chem. Zentr., 1937, i, 3493; cf. A., 1933, 288).—Dithiocamphorimide, m.p. 135° , $\text{NH}_2\text{OH}\cdot\text{HCl}$, and aq. Na_2CO_3 give *thiocamphorimideoxime* (I), m.p. 180° (decomp. 235°) (*Ac* derivative, m.p. 177°), and *camphorimidedioxime*, m.p. 250° (decomp. 265°). (I) is oxidised (alkaline KMnO_4) to camphorimide, which does not react with NH_2OH .

H. B.

Stereoisomeric camphorylideneacetic acids. H. RUPE and O. KLEMM (Helv. Chim. Acta, 1938, 21, 1532-1538).—Condensation of camphorquinone with $\text{CH}_2\text{Br-CO}_2\text{Et}$ in presence of well-amalgamated Mg (Zn is ineffective) gives *Et* β -hydroxyisocamphorylacetate (I), b.p. $172^\circ/13$ mm. (*Ac*, b.p. $182-184^\circ/13$ mm., and non-homogeneous Bz, b.p. $197-201^\circ/13$ mm., derivatives), with a neutral *by-product*, $\text{C}_{15}\text{H}_{20}\text{O}_4$, m.p. $178-179^\circ$, which contains 2 OH (Zerevitinov), gives a compound, $\text{C}_{32}\text{H}_{36}\text{O}_9\text{N}_2$, m.p. 147° , with $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ and $\text{C}_5\text{H}_5\text{N}$, and is oxidised by KMnO_4 to camphoric acid. (I) is hydrolysed to the

very stable β -hydroxyisocamphorylacetic acid, b.p. 212—225°/13 mm. (slight decomp.), which is best dehydrated by treatment with PBr_3 in C_6H_6 followed by heating the mixture alone and with KOH-MeOH to *trans*-isocamphorylideneacetic acid (II), b.p. 182—186°/13 mm. The chloride, *p*-toluidide, and Et ester obtained from (II) are identical with those derived from Claisen's *cis*-isocamphorylideneacetic acid (III). The consideration of (II) as the *trans*-form is based on the impossibility of hydrogenating it in presence of Ni or Pd under pressures up to 90 atm., whereas (III) is easily and completely hydrogenated (Ni at room pressure). (II) is oxidised ($\text{KMnO}_4\text{-Na}_2\text{CO}_3$) to camphorquinone. H. W.

Anomalous mutarotation of salts of Reychler's acid. VI. Synthesis and structure of the sultam of 2-N-methylamino-*d*-camphane-10-sulphonic acid. R. L. SHRINER, J. A. SHOTTON, and H. SUTHERLAND (J. Amer. Chem. Soc., 1938, 60, 2794—2796; cf. A., 1938, II, 331).—The anhydro-amide (I) (Armstrong and Lowry, J.C.S., 1902, 81, 1448) with H_2 -Raney Ni in warm 95% EtOH at 3 atm. gives the homogeneous sultam, m.p. 181—182°, $[\alpha]_D^{25} -33^\circ$ in CHCl_3 , of 2-amino-*d*-camphane-10-sulphonic acid, the Na derivative of which with MeI gives the N-methyl-sultam, m.p. 80°, $[\alpha]_D^{25} -59.6^\circ$ in CHCl_3 , hydrolysed by hot, conc. HCl to



verted into 2-methylimino-*d*-camphor-10-sulphonic acid, which with H_2 -PtO₂ in EtOH gives the α -[= (II)] and β -, decomp. 338—343°, $[\alpha]_D^{25} +38.8^\circ$ in EtOH, forms of (II). The structure of the sultams and of (I) is thus proved. R. S. C.

Triterpenes. XLI. Oxidation of betulin monoacetate by chromium trioxide to acidic products. L. RUZICKA, A. H. LAMBERTON, and E. W. CHRISTIE (Helv. Chim. Acta, 1938, 21, 1706—1717).—Betulin monoacetate is oxidised by CrO_3 in AcOH at 20°, the products are dissolved in Et₂O, and the solution is shaken successively with aq. Na_2CO_3 and NaOH. Crystallisation from EtOAc of the mixture of acids obtained by acidifying the Na_2CO_3 extract leads to the isolation of "acetyldicarboxylic acid E," $\text{C}_{29}\text{-}_{30}\text{H}_{48}\text{-}_{50}\text{O}_5$, m.p. 339—340°, $[\alpha]_D +20.6^\circ$ in CHCl_3 (Me_2 ester, m.p. 243—245°, $[\alpha]_D +19^\circ$ in CHCl_3), which is indifferent towards Ac_2O and is hydrolysed (KOH-EtOH) to "dicarboxylic acid E" (I) (Me ester, m.p. 245—246°). The compounds do not give a colour with $\text{C}(\text{NO}_2)_4$. The EtOAc mother-liquor contains "acetyldicarboxylic acid A" (II), which is not readily isolated and is therefore hydrolysed to dicarboxylic acid A, $\text{C}_{29}\text{H}_{48}\text{O}_5$, m.p. 338—340°, $[\alpha]_D -53^\circ$ in dioxan (Me_2 ester, m.p. 179—181°, $[\alpha]_D -57^\circ$ in CHCl_3), which appears to yield an amorphous anhydride. Acidification of the NaOH extract liberates the monobasic acetylbetulic acid (III), $\text{C}_{32}\text{H}_{50}\text{O}_4$, m.p. 288—290°, $[\alpha]_D +20.1^\circ$ in CHCl_3 (Me ester, m.p. 200—202°, $[\alpha]_D +17.1^\circ$ in CHCl_3), hydrolysed and then esterified to *Me betulate*, m.p. 224—226°, $[\alpha]_D +5.0^\circ$ in CHCl_3 . Hydrogenation (PtO_2 in

AcOH) of (III) gives acetyldihydrobetulic acid (Me ester, m.p. 238—239°), identical with the product obtained by the oxidation of dihydrobetulin monoacetate (work to be published later). Oxidation of (III) by CrO_3 in AcOH gives (I) and (II), each in about 10% yield; (III) is therefore an intermediate product in the formation of (I) and (II). All m.p. are corr. H. W.

Triterpenes. XLII. Keto-derivatives of oleanolic acid. L. RUZICKA, S. L. COHEN, M. FURTER, and F. C. VAN DER SLUYS-VEER (Helv. Chim. Acta, 1938, 21, 1735—1746).—Decarboxylation of acetylketo-oleanolic acid (I) (Kitasato, A., 1934, 412; Ruzicka and Cohen, A., 1937, II, 382) in boiling quinoline leads smoothly to a neutral compound (III), $\text{C}_{31}\text{H}_{46}\text{O}_3$, m.p. 208—210°, which gives a marked yellow colour with $\text{C}(\text{NO}_2)_4$ in CHCl_3 and does not show the absorption spectrum typical of an $\alpha\beta$ -unsaturated ketone. Comparison of the absorption curves of $\Delta^{1:4}$ -cholestadien-3-one, phorone, $\Delta^{1:6}$ -androstadiene-3:17-dione, santonin, dimethylquinol, and (II) does not decide whether it is possible to distinguish spectrographically between a ketone with double linkings at each side of CO and one containing two conjugated double linkings on one side. isoAcetylketo-oleanolic acid (II), m.p. 328—330°, $[\alpha]_D +61^\circ$ in CHCl_3 (cf. Kitasato, A., 1935, 1126), best obtained from acetylketo-oleanololactone and HBr in boiling EtOH, appears from its absorption spectrum to contain the $\alpha\beta$ -unsaturated CO group; this view is supported by the impossibility of detecting the double linking or CO in the usual manner. It is reduced (Clemmensen) to isoacetyloleanolic acid, m.p. 280—282°, $[\alpha]_D +75^\circ$ in CHCl_3 , which gives a yellow colour with $\text{C}(\text{NO}_2)_4$. (II) passes in boiling quinoline into a substance, $\text{C}_{32}\text{H}_{48}\text{O}_5$, m.p. 277—279°. (I), new m.p. 272—273° (Me ester, new m.p. 252—253°), is converted by KOH-MeOH into keto-oleanolic acid (III), m.p. 264—265° [Me ester (III), m.p. 196—197°]. The rates of hydrolysis of Me oleanonate, acetyloleanolate, acetylketodihydro-oleanolate, acetylketo-oleanolate, (III), and Me isoacetylketo-oleanolate have been compared. Theoretical discussion of the results leads to a preference for Haworth's modification of the C skeleton of triterpenes of the oleanolic acid type (Ann. Repts., 1937, 34, 327 seq.). H. W.

Structure of some triterpenes. G. GIACOMELLO (Atti R. Accad. Lincei, 1938, [vi], 27, 574—578).—From a discussion of X-ray data for various triterpenes it is concluded that these have a structure analogous to that of the hydrocarbon $\text{C}_{24}\text{H}_{38}$ obtained by dehydrogenation of triterpenes. O. J. W.

Structure of lignin. A. B. CRAMER, M. J. HUNTER, and H. HIBBERT (J. Amer. Chem. Soc., 1938, 60, 2813).—The ketone, $\text{C}_{13}\text{H}_{18}\text{O}_4$ (2:4-dinitrophenylhydrazones, m.p. 134—136°) (A., 1938, II, 449), is identified as 4- α -ethoxypropioveratrone (I) by synthesis by the following steps: veratrole + $\text{EtCOCl} \rightarrow$ 4-propioveratrone \rightarrow the α -Br-derivative \rightarrow 1:2:4-(OMe)₂C₆H₃CO-CHMeOAc \rightarrow (I) + the derived OH-compound. R. S. C.

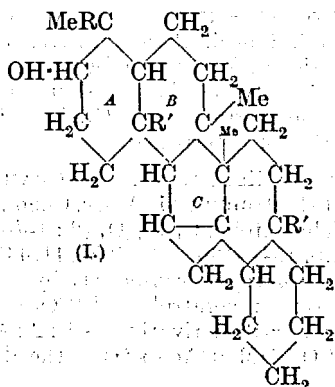
Structure of lignin. M. J. HUNTER, A. B. CRAMER, and H. HIBBERT (J. Amer. Chem. Soc.,

1938, 60, 2815—2816).—Solvent extraction of maple wood gives the known ketones, $C_{12}H_{16}O_4$ and $C_{13}H_{18}O_5$ (*p*-nitrobenzoate, m.p. 141—142.5°) (A., 1938, II, 449), in about equal amounts. R. S. C.

Dihydroabiatic acids from so-called pyroabiatic acids. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1938, 60, 2621—2622).—A *dihydroabiatic acid*, m.p. 174—176°, $[\alpha]_D^{20} +108^\circ$ in EtOH, is isolated from α -pyroabiatic acid. The " H_2 -acid," $[\alpha]_D^{20} -3^\circ$ (A., 1938, II, 239), is the lactone of Hasselstrom *et al.* (*ibid.*, 288). R. S. C.

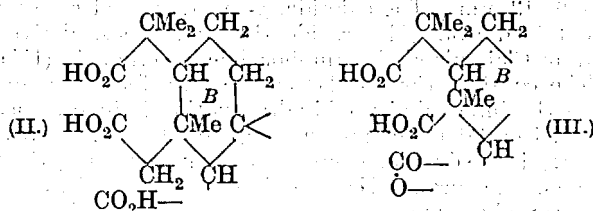
Substitution reactions of dehydroabiatic acid. L. F. FIESER and W. P. CAMPBELL (J. Amer. Chem. Soc., 1938, 60, 2631—2636).—Sulphonation of pyroabiatic acid (prepared by Pd) at -5° to sulphodehydroabiatic acid (I), $+0.5H_2O$, m.p. variable, 247—248° (decomp.), $[\alpha]_D^{25} +72.4^\circ$ [*p*- $C_6H_4Me.NH_2$ salt, m.p. 271° (decomp.), $[\alpha]_D^{25} +57^\circ$ in EtOH], and hydrolysis thereof by acid at 135° gives a 42—43% over-all yield of dehydroabiatic acid (II). With NaOH at 280—300° (I) gives a mixture of acids, (III), m.p. 196.5—197.5°, and (IV), m.p. 167—169°. With Se (III) gives 68% of retene; (III) gives *anilides*, m.p. 255.5—257° and 114—114.5°, of acids, $C_{19-20}H_{24-28}O_3$ and $C_{19}H_{22}O_2$, respectively. (IV) gives *anilides*, m.p. 214—215° and 147.5—148°, the latter derived from an acid, $C_{19}H_{26}O_2$. The *anilides* resisted hydrolysis. The Me at $C_{(12)}$ is probably partly removed during the alkali fusion. No $(NO_2)_1$ -derivative of (I) could be prepared; only the known (? 6 : 8)-dinirodehydroabiatic acid was formed. With AcCl and $AlCl_3$ in $PhNO_2$ at 0—5° the Me ester of (II) gives *Me 6-acetyldehydroabietate*, forms, m.p. 133.5—134° and 119.5—120°, $[\alpha]_D^{25} +56^\circ$ in EtOH (*oxime*, m.p. 151.5—152°, $[\alpha]_D^{25} +83^\circ$ in EtOH), converted by HNO_3 into 1 : 2 : 4 : 5- $C_6H_2(CO_2H)_4$, by I-KI into *Me 6-carboxydehydroabietate*, m.p. 190—191.5°, $[\alpha]_D^{25} +74^\circ$ in EtOH, and by KOH-EtOH into 6-acetyldehydroabiatic acid, m.p. 174.5—175°, $[\alpha]_D^{25} +74^\circ$ in EtOH. M.p. are corr. R. S. C.

Constitution of acid sapogenins. XIV. Hederagenin and oleanolic acid. Z. KITASATO (Acta Phytochim., 1938, 10, 239—258).—On the basis of the following and published work oleanolic acid ($R = Me$) and hederagenin ($R = CH_2.OH$) are considered

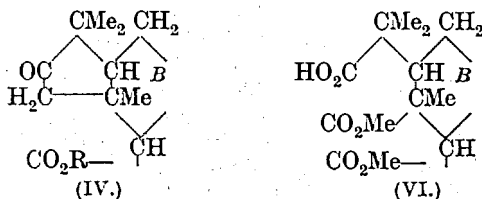


to be (I), ($R' = CO_2H$ or Me ; $R'' = Me$ or CO_2H). Monobromo-oleanolactone and CrO_3 -AcOH give

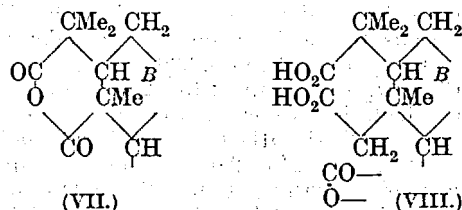
oleanoltri-acid (II), $C_{30}H_{46}O_6$, $+0.5EtOH$, m.p. 294—296° (decomp.), and oleanintri-acid (III), $C_{29}H_{44}O_6$, $+AcOH$, m.p. 272—275° (decomp.) (cf. A., 1937, II, 462, which is also corr. in other respects below). (II) closely resembles hederatri-acid, whereas (III)



usually reacts differently. The Me_3 ester, m.p. 167—168°, of (II), is converted by KOH-MeOH into the Me keto-ester (IV) ($R = Me$), new formula $C_{30}H_{46}O_3$, m.p. 183—185° (*oxime*, m.p. 215—216°), which with $HBr-AcOH-CHCl_3$ at room temp. (1 week) yields a *lactone* (V), $C_{29}H_{44}O_3$, m.p. $>350^\circ$, the trimethylene ring having been converted into an ethylenic linking which lactonises with the CO_2H . However, the Me_3 ester, m.p. 183°, of (III) is hydrolysed by KOH-MeOH to the acid ester (VI), m.p. 222—224°. At about 340° (II) gives the *keto-acid* (IV) ($R = H$), $C_{29}H_{44}O_3$, m.p. 300° (decomp.), and hederatri-acid gives the similar

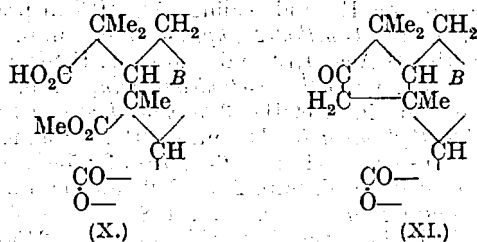


ketone, $C_{26}H_{40}O$, m.p. 205—207° (*oxime*, m.p. 199—200°); however, (III) gives the *anhydride* (VII), m.p. 222°, converted by hydrolysis and methylation into the Me_3 ester, m.p. 145—147°, of the corresponding acid. With $HBr-AcOH$ this ester gives a mixture, m.p. 155—164°, of a bromodicarboxylate and a lactonic ester, reduced by Zn dust-AcOH to a mixture, m.p. 165—175°, of a dicarboxylate and lactonic ester; a similar mixture, m.p. $>300^\circ$, of the corresponding Br-free acids is also prepared. With $HBr-AcOH$ (II) or its ester gives the *lactone* (VIII), $C_{32}H_{50}O_6$,



$+0.5H_2O$, m.p. 216°, and hederatri-acid gives a monolactone (IX) (Me_2 ester, m.p. 168—170°), but (III) or its ester gives the *monolactone-anhydride*, $C_{29}H_{42}O_5$ [as (VII), but containing a lactone group], m.p. 355—358° [*Me* (X), m.p. 265—267°, and *Et*, ester, m.p. 222°]. At 340° (VIII) gives the *keto-lactone* (XI), $C_{29}H_{44}O_3$, m.p. $>350^\circ$; a *product* (XII), m.p. 285° (*oxime*, m.p. 228—230°), is similarly obtained from (IX), but (X) regenerates the monolactone-anhydride. The Me_3 ester of keto-oleanintri-acid,

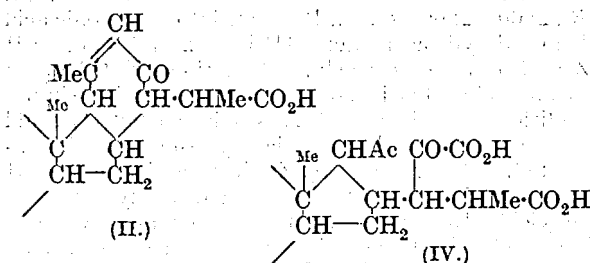
$C_{33}H_{52-54}O_7$, is now regarded as that of keto-oleanol-tri-acid, and the product obtained therefrom by



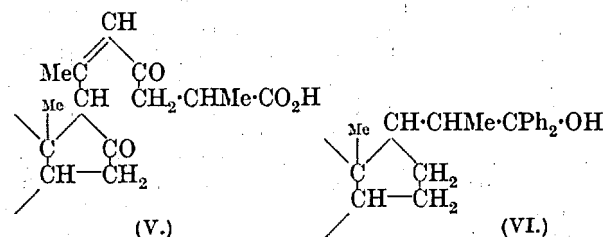
KOH-MeOH is a diketo-monoester, $C_{30}H_{46-48}O_4$, analogous to (IV). R. S. C.

Sarsasapogenin. II. Sarsasapogenoic acid.
III. Deoxysarsasapogenin and the degradation of the C_{22} -hydroxylactone. L. F. FIESER and R. P. JACOBSEN (J. Amer. Chem. Soc., 1938, 60, 2753—2761, 2761—2764; cf. A., 1938, II, 108).—
 II. Improved prep. of sarsasapogenoic acid (I) gives also small amounts of the OH-lactone acetate, $C_{22}H_{33}O_5 \cdot OAc$, and (?) *hydroxysarsasapogenin acetate*, (?) $C_{22}H_{33}O_5$, m.p. 158—160°. With HCl-EtOH- C_6H_6 , Na-Pr^oOH, semicarbazide, or $NH_2OH \cdot EtOH$ (I) gives gums; with NH_2OH at 130° its Me ester gives a *substance*, $C_{25}H_{40}O_5N_2$, m.p. 169—171°, in very poor yield; with $NH_2OH \cdot MeOH$ at 130° (I) gives abnormally an *acid*, $C_{27}H_{44}O_5N_2$, m.p. 247° (decomp.; preheated at 247°). With $H_2 \cdot PtO_2$ in AcOH (I) gives very slowly *anhydro-di- or -tetra-hydrosarsasapogenoic acid*, $C_{27}H_{42-44}O_4$, m.p. 174—178° [Me ester *acetate*, +0.5MeOH.0.5H₂O, m.p. 64—66° (decomp.), and *benzoate*, m.p. 138.5—140.5°]. *Anhydrosarsasapogenoic acid* (II) with $H_2 \cdot PtO_2$ in EtOH or Na-Pr^oOH gives the H_4 -acid (III), m.p. between 179° and 188° [Me ester *diacetate*, m.p. 159.5—161°, also obtained by hydrogenating the oily Me ester of (II)]; absorption (max. at 2430 Å.) proves that (I) is an $\alpha\beta$ -unsaturated ketone, a system suggested by the Na-Pr^oOH reduction. One OH of (III) is at C_3 , the other a new *sec.* OH obtained by reduction of the CO of (II). With boiling Ac_2O or $BzCl \cdot C_5H_5N$ at 55° (III) gives a *lactone acetate*, $C_{29}H_{44}O_4$, m.p. 200—203°, and *lactone benzoate*, m.p. 225—235°, respectively, proving that the new OH is γ or δ in respect to the CO_2H . (II) is thus a γ - or δ -keto-acid. The composition of (II) and the indifference of (III) to H_2 -catalyst and $KMnO_4$ show that (II) contains a new ring. CrO_3 gives only oils from the Me ester acetate of (II), but with alkaline $KMnO_4$ (II) gives a dibasic *keto-acid* (IV), $C_{27}H_{40}O_7$, m.p. 206—207° (decomp.) [Me₂ ester, m.p. 164.5—165°; *anhydro-oxime*, $C_{27}H_{39}O_6N$, m.p. 268° (decomp.)], converted by NaOH into CHI_3 and a trace of a *substance*, $C_{25}H_{36-38}O_7$, m.p. 212—213° (decomp.). These oxidations prove that (II) contains $\cdot CH_2 \cdot CMe$, converted into $CO_2H \cdot X \cdot CMe$. Thus, (II) contains $\cdot CMe \cdot CH \cdot CO \cdot C_2 \cdot CO_2H$, the alternative $\cdot CH \cdot CMe \cdot CO \cdot C_2 \cdot CO_2H$ being incompatible with the cholesterol side-chain. It follows that (I) and thus sarsasapogenin (modified prep.) have the structures suggested by Tschesche and Hagedorn (A., 1935, 1126; 1936, 209). The annexed structures for (II) and (IV) follow. Those of (III) and its lactone are

also certain, and structures (not proved) are suggested for other derivatives. With Zn-Hg-HCl-EtOH (II) gives a *lactone*, $C_{27}H_{42}O_3$, m.p. 226—229° (*acetate*, m.p. 214—216°).



III. Work of Simpson and Jacobs (A., 1935, 1248) is extended. Deoxysarsasapogenin (prep. improved to give a 43.5% yield) and CrO_3 -80% AcOH at 60—65° give the deoxylactone (13%), $C_{22}H_{34}O_2$, m.p. 129.3—130.5°, a *diketo-acid*, $C_{27}H_{40}O_4$, +H₂O (not lost on drying), m.p. 108—111° (Me ester, m.p. 78.5—79.5°; *oxime*, m.p. 189—191° (decomp. from about 178°) [probably (V), although the H₂O of crystallis-



ation may be constitutional], and a trace of an *acid*, m.p. 218—220°. The diphenylcarbinol monoacetate (A., 1938, II, 108) with CrO_3 -AcOH at 20—25° gives a *ketone acetate*, $C_{36}H_{46}O_4$, m.p. 157—159° [indifferent to CO-reagents; OAc at C_3 ; CO as in (V)], reduced by Zn-Hg-HCl-EtOH to a *deoxydiphenylcarbinol* (VI), $C_{34}H_{46}O_2$, m.p. 226—228°. M.p. are corr.

R. S. C.

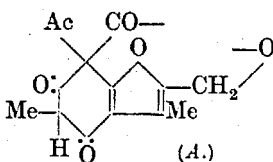
Chondrilla resins. I. K. MATZUREVITSCH (Bull. Sci. Univ. Kiev, 1937, 3, No. 3, 7—28).—The resins consist chiefly of esters, from which *chondrillin* (I), $C_{28}H_{47}OH$, + H₂O, m.p. 187—188° (*acetate*, m.p. 229—230°; *isobutyrate*, m.p. 241—242°; *benzoate*, m.p. 262—263°), is obtained by hydrolysis, together with other alcohols and HCO_2H , AcOH, and a no. of amorphous resinic acids of high mol. wt. (I) has one double linking, and forms a *dibromide*, m.p. 181—182° (*acetate*, m.p. 208—209°; *benzoate*, m.p. 186—189°).

R. T.

Synthesis of 5-hydroxycoumarin. H. A. SHAH and R. C. SHAH (J.C.S., 1938, 1832—1833).—A detailed account of work already noted (A., 1938, II, 451). The following is new: Et 5-hydroxy-6-carbomethoxycoumarin-3-carboxylate is hydrolysed (NaOH) to 5-hydroxycoumarin-3:6-dicarboxylic acid, m.p. 265—267° (efferv.), also obtained from 2:4-dihydroxy-3-formylbenzoic acid and $CN \cdot CH_2 \cdot CO_2H$. 5-Hydroxycoumarin-3-carboxylic acid, m.p. 272—274° (efferv.), is obtained from γ -resorcyaldehyde and $CN \cdot CH_2 \cdot CO_2H$. The m.p. of 5-hydroxycoumarin (Ac

derivative, m.p. 88—89°) is now given as 222—225° (previously 221—223°). F. R. S.

Lichen substances. LXXXIX. Usnic acid. V. Y. ASAHINA and M. YANAGITA (Ber., 1938, 71, [B], 2260—2269; cf. A., 1938, II, 110).—Usnic acid (I) and dihydrous acid (II) have 2 and 3 active H (Zerevitinov) respectively. Oxidation $[\text{Pb}(\text{OAc})_4]$ of *r*-usnic acid affords *r*-usnic acid; under similar conditions *d*-usnic acid (III) is oxidised but (I) could not be isolated whereas diacetylusnic acid is unaffected. (I) is reduced by Zn dust and boiling AcOH to (III). Similar reduction of Et *d*-isooxyacetate yields Et *r*-acetate, the asymmetry being destroyed. *iso*Oxyusnetic acid is reduced to usnetic acid and oxidised (H_2O_2 -KOH) to 4:5-dicarboxy-3-methylfuran-2-acetic acid, m.p. 251—252° (decomp.) after becoming discoloured at about 240°. Usnetic acid is hydrogenated (Pd-black in AcOH) to *dihydro-usnetic acid*, m.p. 214° (*Me* ester, m.p. 161°). *Di-acetyl-d-usnic acid*, m.p. 202°, $[\alpha]_D^{20} + 200.2^\circ$ in CHCl_3 , obtained with a colourless substance, m.p. 132°, by means of Ac_2O containing a little conc. H_2SO_4 at 50°, is converted by 5% Na_2CO_3 into *monoacetyl-d-usnic acid* (IV), m.p. 180—181°, $[\alpha]_D^{20} + 291.5^\circ$ in CHCl_3 , hydrolysed by conc. H_2SO_4 to (III) and transformed by boiling EtOH into its *O*-Et derivative, $\text{C}_{22}\text{H}_{24}\text{O}_9$, m.p. 110° (*semicarbazone*, m.p. 211°); the last compound is transformed by cold conc. H_2SO_4 into Et usniolate, m.p. 175—176°, which gives a green colour with FeCl_3 , and by boiling H_2O or, preferably, boiling 50% AcOH into a substance, $\text{C}_{20}\text{H}_{22}\text{O}_8$, m.p. 153°, which is indifferent towards $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ or $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ but is converted by conc. H_2SO_4 into Et acetate. (IV) is transformed by boiling 60% AcOH into *monoacetyldecarbousnic acid*, m.p. 128°, which gives a violet dye with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$. Diacetyldihydrous acid and 60% AcOH at 130° give *monoacetyldihydrousnic acid*, m.p. 132°, $[\alpha]_D^{20} - 42.09^\circ$ in CHCl_3 , also obtained by means of aq. Na_2CO_3 . Oxidation (KMnO_4 -KOH) of *d*-dihydrous acid and thermal decomp. of the product affords



2:6-dihydroxy-3-methylacetophenone (and a *by-product*, $\text{C}_{11}\text{H}_{18}\text{O}_5$, m.p. 217°), also obtained similarly from diacetyltetrahydrodeoxyusnic acid. Dry distillation of (II) gives 6-hydroxy-7-acetyl-3:5-dimethylcoumaran-2-one (V), m.p. 127° (*monoacetate*, m.p. 101—102°; *p*-nitrophenylhydrazone, m.p. 258°), transformed by alkali at 80° into α -2:4-dihydroxy-3-acetyl-5-methylphenylpropionic acid, m.p. 147° (vigorous decomp.). Reduction (Clemmensen) of (V) yields 6-hydroxy-3:5-dimethyl-7-ethylcoumaran-2-one, m.p. 113°. The coumarone skeleton of (III) is amended to (A).

H. W.

Synthesis of certain products of the decomposition of dihydrous acid. M. YANAGITA (Ber., 1938, 71, [B], 2269—2273).—4:3:1- $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$ (I) is rapidly transformed by ZnCl_2 in boiling AcOH into 5-methylresacetophenone, m.p. 170°. $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, conc. H_2SO_4 , and (I) at 0° yield 7-hydroxy-4:6-dimethylcoumarin, m.p. 254—255° (decomp.) after softening at about 210°. The corresponding

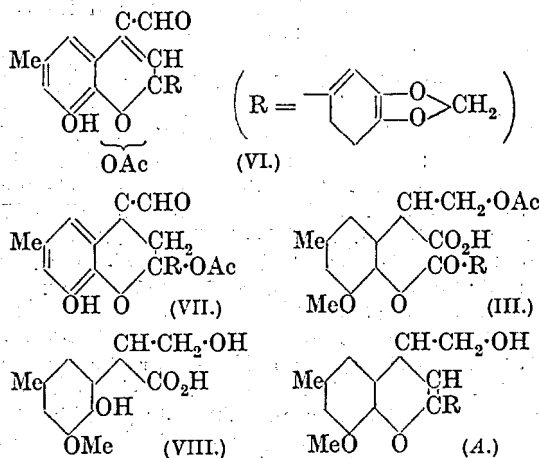
acetate, m.p. 159°, is converted by AlCl_3 at 180° into 2:6-dihydroxy-3-methylacetophenone, m.p. 138°, reduced by Zn-Hg and boiling 15% HCl in presence of PhMe to 4-methyl-2-ethylresorcinol, m.p. 105°. This with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and cold conc. H_2SO_4 affords 7-hydroxy-4:6-dimethyl-8-ethylcoumarin, m.p. 189°, whence (Br in AcOH) 3-bromo-7-hydroxy-4:6-dimethyl-8-ethylcoumarin (II), m.p. 204°. Boiling 10% KOH transforms (II) into 6-hydroxy-3:5-dimethyl-7-ethylcoumarilic acid, m.p. 227—229° (decomp.). The corresponding *Me* ester, m.p. 158°, is transformed successively into the *hydrazide*, decomp. 245—246° after becoming red at 235°, *azide*, decomp. about 135°, and 6-hydroxy-3:5-dimethyl-7-ethylcoumarylurethane, m.p. 140°; this is converted by boiling 10% KOH into NH_3 and α -2:4-dihydroxy-5-methyl-3-ethylphenylpropionic acid, which is anhydridised to 6-hydroxy-3:5-dimethyl-7-ethylcoumaran-2-one, m.p. 113°. H. W.

Stearoptens of orange-peel oil. I. H. BÖHME and G. PIETSCH (Arch. Pharm., 1938, 276, 482—488).—The oil yields a fish-poison, *auraptin* (I), $\text{C}_{15}\text{H}_{18}\text{O}_4$, m.p. 91°, $[\alpha]_D^{20} - 33.4^\circ$ in 96% EtOH, which is a coumarin since it possesses lactonic properties and is hydrogenated (Pd-C) in AcOH or NaOEt-EtOH to *dihydroauraptin*, m.p. 116°, and *dihydroauraptenic acid*, $\text{C}_{15}\text{H}_{20}\text{O}_5$, m.p. 98.5° [oxidised by HNO_3 to $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$], respectively. Coumarin and (I) are stable to $\text{o-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. R. S. C.

Egonol. III. Degradation of acetylegonol by ozone. S. KAWAI and F. YOSHIMURA. **IV. Oxidation of acetylegonol with hydrogen peroxide.** S. KAWAI and N. SUGIYAMA [with, in part, I. TSUBAKI] (Ber., 1938, 71, [B], 2415—2420, 2421—2432; cf. A., 1938, II, 373, 501).—III. Ozonisation of acetylegonol (I) in EtOAc at 0° and treatment of the ozonide with steam gives CH_2O in amount insufficient to suggest the presence of a vinyl group and *acetylstyraxinaldehyde* (II), $\text{C}_{21}\text{H}_{20}\text{O}_8$, m.p. 97—98° [*phenylhydrazone*, m.p. 151° (slight decomp.)], which reduces cold Fehling's solution but does not give the Legal reaction; it is hydrolysed by 2*N*-NaOH at about 80° to piperonylic acid and the non-cryst. *styraxinaldehyde* [*monophenylhydrazone*, $\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}_2$, m.p. 153° (slight decomp.)]. Oxidation of (II) with AcO_2H gives *acetylstyraxic acid* (III), m.p. 168°. *Styraxinolic acid* with Me_2SO_4 -KOH and CH_2N_2 followed by NaOBr gives *isohemipinic acid* (IV), m.p. 248°. *Allylvanillin* is transformed by Me_2SO_4 and KOH into non-cryst. 3:4-dimethoxy-5-allylbenzaldehyde, b.p. 173—175°/24 mm., which does not give a colour with FeCl_3 and is converted by 1:3-dimethylbarbituric acid in 80% EtOH at 100° into 3:4-dimethoxy-5-allylbenzylidenedimethylbarbituric acid, m.p. 110°; it is oxidised (aq. KMnO_4 - C_6H_6 at about 90°) to (IV).

IV. Investigation of benzoylegonol, m.p. 117.5—118°, *p*-nitrobenzoylegonol, m.p. 129—130°, and *egonol-phenylurethane*, m.p. 132—132.5°, establishes the formula $\text{C}_{19}\text{H}_{18}\text{O}_5$ (not $\text{C}_{20}\text{H}_{18}\text{O}_5$) for egonol (V). (I), m.p. 108.5°, is oxidised by 30% H_2O_2 in AcOH to *noregonolonidine acetate* (VI), m.p. 179°, hydrogenated (Pt-black in dioxan) to *dihydronoregonolonidine acetate* (VII), m.p. 185—186°, which is relatively stable when dry but readily autoxidised when dissolved, particularly in AcOH. The mother-liquors from

(VII) contain piperonylic acid and (III), m.p. 168° (*Me* ester, m.p. 104°), which does not give colour



reactions with FeCl_3 or $\text{Cu}(\text{OAc})_2$ in EtOH but readily yields CHI_3 . 2N-KOH transforms (III) into *styraxinolic acid* (VIII), m.p. 171°, which gives an unusually sensitive, dark blue colour with FeCl_3 and is converted by distillation at 200—230°/7 mm. into a substance, $\text{C}_{11}\text{H}_{12}\text{O}_4$ or $\text{C}_{10}\text{H}_{14}\text{O}_3$. *p-Bromophenacyl styraxinolate* has m.p. 137.5—138°. (III) is transformed by successive treatments with SOCl_2 and conc. NH_3 into *acetylstyraxamide*, m.p. 134—135°. (I) is probably A. H. W.

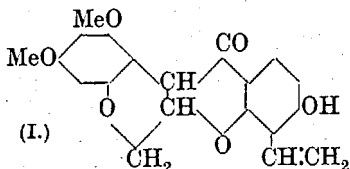
Benzylidenecoumaranones considered as chalcones. T. B. PANSE and T. S. WHEELER (Current Sci., 1938, 7, 181).—A preliminary note.

R. S. C.

Synthesis of linear naphthaflavone. V. V. VIRKAR and T. S. WHEELER (Current Sci., 1938, 7, 181—182).—A preliminary note.

R. S. C.

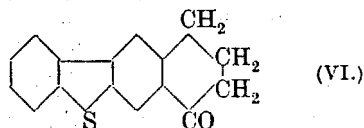
Buckley's substance, m.p. 183°, from *Derris* extract. J. J. BOAM and R. S. CAHN (J.C.S., 1938, 1818—1820).—The substance, m.p. 183°, obtained by Buckley (B., 1936, 1117) appears to be homogeneous and analysis of the solvent-free crystals and the *solvate* ($+0.5\text{C}_6\text{H}_6$) agrees best with $\text{C}_{20}\text{H}_{16}\text{O}_6$, or less well with $\text{C}_{20}\text{H}_{18}\text{O}_6$. The structure (I) is suggested and the substance is held not to occur naturally as such but to be derived by degradation of deguelin by the alkali used in its isolation.



F. R. S.

Dibenzthiophen: orientation and derivatives. H. GILMAN and A. L. JACOBY (J. Org. Chem., 1938, 3, 108—119).—Dibenzthiophen (I) (prep. in 65—70% yield from Ph_2S and AlCl_3 at 115—240°), m.p. 99°, gives (Friedel-Crafts) 3-acetyldibenzthiophen, m.p. 111° (*oxime*, m.p. 160—161°), oxidised by I-KI-NaOH to the 3-carboxylic acid (*Me* ester, m.p. 74—75°). When treated with LiBu^a , LiPh , $\text{LiC}_{10}\text{H}_7$, or

$\text{LiC}_6\text{H}_4\text{-OMe-}p$ and then with CO_2 (I) gives 55, 12, 7.6, and 0%, respectively, of *dibenzthiophen-1-carboxylic acid*, m.p. 252—253° (*Me* ester, m.p. 95°; decarboxylated by Cu in quinoline at 120—200°). When treated with LiBu^a and then with Me_2SO_4 (I) gives 1-methyldibenzthiophen, m.p. 65.5°, also obtained from 2:2'-dihydroxy-3-methyldiphenyl by P_2S_5 at 165—400°. The Li derivative (II) of (I) with MgEtCl and O_2 at $<3^\circ$ gives 1-hydroxydibenzthiophen (III), m.p. 167° [$(\text{NO}_2)_2$ -derivative, m.p. 204° (decomp.); *Me* ether, m.p. 123°]. Br converts (II) into the 1-Br-compound, which with aq. NH_3 and CuBr at 200—200° gives 1-aminodibenzthiophen, m.p. 110° [also obtained from (III) by aq. NH_3 and NaHSO_3 at 200—210°], the Ac derivative, m.p. 198°, of which gives 4-bromo-1-acetamidodibenzthiophen, m.p. 254°, and thence 4-bromo-1-amino-, m.p. 156°, and 4-bromodibenzthiophen (IV), m.p. 84° (1:1-dioxide, m.p. 170—171°). By the Grignard reagent (IV) gives *dibenzthiophen-4-carboxylic acid*, m.p. 176—177° (*Me* ester, m.p. 72—72.5°). Mercuration of (I) occurs at 140—150° (not in EtOH), but gives a mixture, m.p. 215° (decomp.). 3-Acetamidodibenzthiophen, m.p. 178° (lit., 168°), is obtained from (I) by nitration etc., from the 3-Br-compound by $\text{NH}_3\text{-CuBr}$, and by Beckmann rearrangement (PCl_5) of the appropriate amine; it yields a NO_2 -derivative, m.p. 250° (decomp.), and thence, by HCl-EtOH , MeCHO and a N-free compound, m.p. 88°. With Na in liquid NH_3 , followed by NH_4NO_3 , (I) gives 1:4-dihydrodibenzthiophen (V), m.p. 76° (*picrate*, m.p. 105°). The dibromide of (V) loses 2HBr to yield (I); with LiPh it gives (I), C_6H_6 , and LiH , and is also dehydrogenated by other very reactive organoalkali compounds. With $(\text{CH}_2\text{-CO})_2\text{O}$ and AlCl_3 in $\text{C}_2\text{H}_5\text{Cl-PhNO}_2$ (I) gives γ -keto- γ -3-dibenzthiophenylbutyric acid, m.p. 160.5—161°, reduced by Zn-Hg in aq. HCl-PhMe-AcOH to γ -3-dibenzthiophenylbutyric acid, m.p. 131°, which is cyclised by 88% H_2SO_4 to (?) 1-keto-1:2:3:4-tetrahydro- β -thiobrazan (VI), m.p. 178°.



With $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and AlCl_3 (I) gives 3-*o*-carboxybenzoyldibenzthiophen, m.p. 105—106°, converted by NaCl-AlCl_3 at 100—150° into *thionaphtheno-1:2:2:3(or 1:2)-anthraquinone*, m.p. 285—286°.

R. S. C.

Relative reactivities of organometallic compounds. XVIII. Selective metalations of dibenzthiophen. H. GILMAN, A. L. JACOBY, and H. A. PACEVITZ (J. Org. Chem., 1938, 3, 120—124; cf. A., 1937, II, 528).—In contrast to other organometallic compounds (preceding abstract) CaPhI attacks C_{12} of dibenzthiophen. Treatment with CO_2 gives *dibenzthiophen-2-carboxylic acid*, decomp. 300—305° (*Me* ester, m.p. 129—130°), decarboxylated by Cu in quinoline at 200°. Dibenzthiophen *SS*-dioxide (modified prep.), m.p. 232°, with HNO_3 (d 1.5) in $\text{H}_2\text{SO}_4\text{-AcOH}$ at 4° gives the 2- NO_2 -derivative, m.p. 265—266° [further nitrated to the known 2:7- $(\text{NO}_2)_2$ -compound], reduced (Sn-HCl) to the 2- NH_2 -

dioxide, m.p. 259—260°, which yields 2-bromodibenzthiophen SS-dioxide, m.p. 224—225° (loses the Br when reduced). R. S. C.

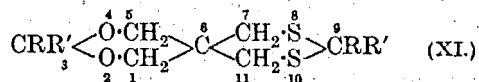
Isosteric compounds. I. Acyl derivatives of dibenzthiophen. A. BURGER, W. B. WARTMAN, jun., and R. E. LUTZ (J. Amer. Chem. Soc., 1938, 60, 2628—2630).—Since S in rings is in many respects similar to CH₂, dibenzthiophen (I) and phenanthrene are said to be isosteric. With AcCl and AlCl₃ in CS₂ (I) gives 3-acetyl- (II), m.p. 111—112° [semicarbazone, m.p. 234—235° (decomp.)], and a little x-acetyl-, m.p. 129—130° [semicarbazone, m.p. 302—304° (decomp.)], and 3:6-diacetyl-dibenzthiophen (III), m.p. 208—209° [obtained similarly from (II) in 90% yield]. The structure of (II) is proved by conversion of its oxime, m.p. 161—164°, by HCl-AcOH-Ac₂O into the known 3-NHAc- and 3-NH₂-compounds, and that of (III) by similar conversion of its dioxime, m.p. 272—274° (decomp.), into the 3:6-(NHAc)₂- and -(NH₂)₂-compounds. (II) forms the main product at 0°, (III) at the b.p. R. S. C.

Some 1:3-dithiols and derived cyclic thioacetals. H. J. BACKER and A. F. TAMSMA (Rec. trav. chim., 1938, 57, 1183—1210; cf. A., 1934, 900, 901; 1937, II, 267, 318).—1:1-Bisbromomethylcyclohexane (I) and K₂S-EtOH for 24 hr. (on bath) afford 2-thia-4-spiroonane (II), b.p. 96°/18 mm. [mercuri-chloride, m.p. 161° (some decomp.) and -bromide, m.p. 157.5°; -2-sulphone, m.p. 72.5—73°; -2-sulphoxide, b.p. 148—151°/5 mm. (mercuri-chloride, m.p. 161.5°)], converted by MeI into γ-iodo-β-pentamethylenepropyldimethylsulphonium iodide, m.p. 92° (picrate, m.p. 117°), and by I-AcOH into 2-thia-4-spiroonane 2:2-dioxide, m.p. 83—84°. (I) refluxed with Na₂S₂-EtOH for 3 hr. gives (II) and 2:3-dithia-5-spirodecane (III), b.p. 136°/11 mm., 147°/17 mm. (mercuri-chloride, m.p. 91°), and some (I). (I) and Na₂S₄-EtOH-H₂O afford (II), (III), and the 2:3:3-trisulphide, b.p. 152°/5 mm. (impure); the latter (b.p. 130—152°/5 mm.) boiled with Cu-PhMe for 20 min. gives (III). (III) is oxidised (H₂O₂) in AcOH to β-pentamethylenepropene-αγ-disulphonic acid (+4H₂O) [Na salt (+4H₂O); Tl salt (+2H₂O)], purified through the Ba salt (+4H₂O). (III) is reduced cold in Et₂O by anhyd. NH₃-Na to αγ-dithiol-β-pentamethylenepropene (IV), b.p. 136°/17 mm. (Hg salt, decomp. 140°). Its Na salt and I-EtOH yield (III). (IV) with aldehydes and ketones, and HCl, gives the following derivatives of

2:4-dithia-6-spiroundecane, [CH₂]₅·C¹₂²CH₂³S⁴CH₂⁵·C⁶₂⁷CH₂⁸S⁹CH₂¹⁰·

3-methyl- (-2:4-disulphone, m.p. 220—221°); 3-phenyl-, m.p. 162°; 3-furyl-, m.p. 103°; 3:4'-1'-hydroxy-2'-methoxyphenyl-, m.p. 191—192°; 3:3-dimethyl-, m.p. 76—77° (dimeride, m.p. 215°) (-2:4-disulphone, m.p. 268.5—269.5°); 3-methyl-3-ethyl-, m.p. 37—37.5°; 3-phenyl-3-methyl- [disulphone, m.p. 293° (decomp.), colours from 265°]; 3:3-diphenyl-, m.p. 125°; 3:3-tetra-, m.p. 68—68.5°, and -penta-, m.p. 106—106.5°, -methylene-; compounds from (IV) and fluorenone, m.p. 172—173°, and from behenone, CO(C₂₁H₄₃)₂, m.p. 63—64°. CMe₂(CH₂Br)₂ and Na₂S₄ (Na₂S₂) in EtOH for 4

(10) hr. give 1:2-dithia-4:4-dimethylcyclopentane (V), b.p. 84—86°/17 mm. (cf. Backer and Evenhuis, loc. cit.) (mercuri-chloride, m.p. 102°), and its 1-thio-derivative (VI), b.p. 117—118°/14 mm.; the latter yields (V) with Cu-PhMe. (VI) and anhyd. NH₃-Na-Et₂O afford αγ-dithiol-β-dimethylpropane, b.p. 72°/12 mm., converted by aldehydes and ketones (HCl gas) into derivatives of 1:3-dithia-5:5-dimethylcyclohexane: parent substance from CH₂O (-1:3-disulphone, m.p. 201°); 2-furyl-, m.p. 62—63.5°; 2:4'-(1'-hydroxy-2'-methoxyphenyl)-, m.p. 170—171°; 2:2-dimethyl-, m.p. 57.5—58.5° (-1:3-disulphone, m.p. 263.5—264.5°); 2-phenyl-2-methyl-, m.p. 59—60°; 2:2-diphenyl-, m.p. 89.5—90.5°; 2:2-pentamethylene- (-1:3-disulphone, m.p. 235.5—237°); thioacetal from fluorenone, m.p. 144.5—145°. (OH·CH₂)₂C(CH₂Br)₂ and Na₂S₄ (or Na₂S₂)-EtOH for 3 hr. afford 1:2-dithia-4:4-bishydroxymethylcyclopentane (VII), m.p. 129—130°, oxidised by H₂O₂-AcOH to β-bishydroxymethylpropane-αγ-disulphonic acid (+3H₂O) [Ba (+3H₂O), Tl (+H₂O), and Na (+3H₂O), salts] and a little 1:2-disulphone, m.p. 242—244° corresponding with (VII). (VII) and anhyd. NH₃-Na afford β-bishydroxymethyl-αγ-bis-thiolmethylmethane (VIII), m.p. 97—98° (cryst. form examined), its Na salt and I-EtOH giving (VII). (VIII) and aldehydes and ketones, with HCl, yield derivatives of 1:3-dithia-5:5-bishydroxymethylcyclohexane: 2-methyl-, m.p. 122—124° (-1:3-disulphone, m.p. 216—219°); 2-phenyl- (IX), m.p. 209—211° [diacetate, i.e., 5:5-(CH₂·OAc)₂, m.p. 134—136°]; 2:4'-(1'-hydroxy-2'-methoxyphenyl)-, m.p. 186.5—188°; 2:2-dimethyl-, m.p. 199.5—200.5°; 2-phenyl-2-methyl- (X), m.p. 164—165° (-1:3-disulphone, m.p. 290°); 2:2-diphenyl-, m.p. 169—170°; 2:2-pentamethylene-, m.p. 186.5—187.5°; 4-methyl-, m.p. 182°, and 4-chloro-, m.p. 194—196°, -pentamethylene-; thioacetals from (VIII) and camphor, m.p. 155—157° and from fluorenone, m.p. 244—245°. (VIII) and PhCHO-EtOH, refluxed for 3 hr., afford 3:9-diphenyl-2:4-dioxa-8:10-dithia-6-spiroundecane [(XI), R = H, R' = Ph], m.p. 171.5—173.5°. (VIII) and excess of COMe₂-HCl gas give 30% of the 3:3:9:9-tetramethyl analogue, m.p. 127—128°, and 60% of



thioacetal (loc. cit.). (X) and CPhMe-HCl-C₆H₆, boiled for 10 hr., yield the 3:9-dimethyl-3:9-diphenyl derivative, m.p. 135—137°, of (XI). 1:3-Dithia-2-methyl-5:5-bishydroxymethylcyclohexane (loc. cit.) and PhCHO in boiling C₆H₆, with HCl gas, give 3-phenyl-9-methyl-2:4-dioxa-8:10-dithia-6-spiroundecane, (XII), m.p. 132—133°. Similarly (IX) and MeCHO-HCl-Na₂SO₄ for 24 hr. afford the 9-phenyl-3-methyl isomeride, m.p. 156—158°. The thioacetal, m.p. 182° (loc. cit.) from 4-methylcyclohexane, with PhCHO-HCl-C₆H₆ for 1 hr., yields 3-phenyl-9-(4-methylpentamethylene)-2:4-dioxa-8:10-dithia-6-spiroundecane, m.p. 126—143°, composed of two isomerides, m.p. 123—125° and 158—160°, possibly *cis*- and *trans*-. 2-Methyl-5:5-bishydroxymethylcyclohexane-1:3-disulphone and PhCHO-HCl-C₆H₆ give 3-phenyl-9-methyl-2:4-dioxa-6-spiro-

undecane-8:10-disulphone, m.p. 229—231°, also obtained from (XII) and $\text{BzO}_2\text{H} \cdot \text{CHCl}_3$. $\text{C}(\text{CH}_2\text{OH})_4$ and $\text{COPhMe} \cdot \text{HCl}$ in boiling xylene for 4 hr. give 3:9-diphenyl-3:9-dimethyl-2:4:8:10-tetraoxa-6-spiroundecane, m.p. 146.5—147.5°. A. T. P.

Synthesis of oxypoline (γ -hydroxypyrrolidine- α -carboxylic acid). V. FEofilAKTOV and A. ONISCHTSCHENKO (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 133—135).— δ -Chloro- α -acetyl- γ -valerolactone yields with aq. NaNO_2 and dil. H_2SO_4 the oxime acetate, m.p. 115—116°, and with PhN_2Cl the phenylhydrazone, m.p. 185—186°, of δ -chloro- α -keto- γ -valerolactone. Reduction ($\text{Sn} + \text{HCl}$) of either of these yields δ -chloro- α -amino- γ -hydroxyvaleric acid, having two forms, one of which, m.p. 165.5—166.5°, with aq. NH_3 yields (via the Cu salt) the *b*-form, and the other the *a*-form, of oxypoline. Leucine is similarly prepared from $\text{CHAcBu}^a \cdot \text{CO}_2\text{Et}$. A. Li.

Exchange of hydrogen atoms between pyrrole, indole, and their methyl derivatives, and water. V. Exchange of hydrogen atoms between *N*-methylindole and water. M. KOIZUMI, Y. KOMAKI, and T. TITANI (Bull. Chem. Soc. Japan, 1938, 13, 643—651).—Exchange of H between molten *N*-methylindole and aq. D_2O at 60° does not occur at $p_{\text{H}} > 2.5$. At $p_{\text{H}} < 2.5$ exchange proceeds rapidly, the β -H being substituted; there is no evidence of exchange with the α -H as is the case with indole (cf. A., 1938, I, 318). J. D. R.

Oxidation products of pyrrole amines. I. T. AJELLO (Gazzetta, 1938, 68, 602—608).—4-Amino-2:3:5-triphenylpyrrole (new prep., reducing the N-OH compound by Al-EtOH) is oxidised by $\text{FeCl}_3 \cdot \text{AcOH}$ to triphenylpyrroleninyldihydroxylamine, $\text{N} \begin{smallmatrix} \text{CPh} \cdot \text{CH} \cdot \text{NH} \cdot \text{OH} \\ \text{CPh} \cdot \text{CPh} \end{smallmatrix}$ (I), m.p. 168° (cf. A., 1937, II, 30) (Ac derivative, m.p. 150°; picrate, m.p. 177°); by $\text{H}_2\text{O}_2 \cdot \text{AcOH}$ to (I) and a substance, m.p. 210°; by $\text{CrO}_3 \cdot \text{AcOH}$ to (I) and a substance, m.p. 290° (also obtained from oximinotriphenylpyrrole; cf. A., 1936, 997); by $\text{K}_3\text{Fe}(\text{CN})_6$ to a compound (II), m.p. 170° (reduced to aminotriphenylpyrrole), and a compound, m.p. 256°; and by PbO_2 to (II).

E. W. W.

Synthesis of compounds exciting parasympathetic nerves. Methyl *N*-methylisonicotinate and its tetra- and hexahydro-derivatives. J. V. SUPNIEWSKI and M. SERAFINÓWNA (Arch. Chem. Farm., 1936, 3, 109—118; Chem. Zentr., 1937, ii, 73—74).—*iso*Nicotinic acid is quantitatively esterified by $\text{MeOH} \cdot \text{H}_2\text{SO}_4$ (unlike nicotinic or picolinic acids), the ester converted into *Me isonicotinate methiodide*, m.p. 183—184°, and then reduced (Pt) to *Me N-methyltetrahydro-*, m.p. 130—131°, and *Me N-methylhexahydro-isonicotinate hydriodide*, m.p. 154—155°. *Me N-methyltetrahydro-* and *N-methylhexahydroisonicotinate*, b.p. 138°/32 mm., and their methiodides, m.p. 152—153°, 193—194°, respectively, were also prepared. The arecoline-like action of these esters which depends on the NMe group is described. A. H. C.

Ethyl acetonedicarboxylate. II. G. JACINTI (Gazzetta, 1938, 68, 592—595).—The semioxamazone, $(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2\text{C} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$, m.p. 116°, of Et

acetonedicarboxylate (I) gives, with 20% aq. NH_3 , 2-hydroxy-6-ethoxy-4-pyridonesemioxamazone, m.p. 274°. The thiosemicarbazone, m.p. 118°, of (I) and aq. NH_3 give, however, 2-hydroxy-6-ethoxy-1:4-pyrone-thiosemicarbazone (?), m.p. 133° (insol. Cu , Ag , Pb salts), also obtained by the action of conc. H_2SO_4 ; the corresponding semicarbazone, m.p. 128° is obtained similarly (also by heating; cf. A., 1938, II, 42). The structure of 2:4-dihydroxy-4-pyridonesemicarbazone (II) (*loc. cit.*) is confirmed by boiling (II) with conc. HCl , and converting the product into the known phenylhydrazone. E. W. W.

Action of sulphuryl chloride on pyridine oxide. R. BOBRANSKI, L. KOCHAŃSKA, and A. KOWALEWSKA (Ber., 1938, 71, [B], 2385—2388; cf. A., 1938, II, 201).— $\text{o-CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ and $\text{C}_5\text{H}_5\text{N}$ in Et_2O give a ppt. of pyridine oxide phthalate, m.p. 122—123°, transformed by 10% HCl into pyridine oxide hydrochloride, m.p. 180° (overall yield 75%). This does not react with SO_2Cl_2 at room temp. or the b.p. but at 120° gives a mixture of 2- and 4-chloro- and penta-chloro-pyridine. The Cl_2 -compounds are separated from one another through their additive compounds with HgCl_2 . H. W.

Nitration of halogen derivatives of pyridine. E. PŁAŻEK, A. SOROKOWSKA, and D. TOŁOPKA (Rocz. Chem., 1938, 18, 210—216).— KNO_3 in conc. HNO_3 , added to 3-halogenopyridines in 10% oleum at 270°, yields 3-chloro-, m.p. 88°, 3-bromo-, m.p. 110°, and 3-iodo-5-nitropyridine, m.p. 198°. The orientation of these compounds is determined by reduction to NH_2 -compounds, of which 3-iodo-5-aminopyridine, m.p. 70° (picrate, m.p. 252°), is new. Under similar conditions of nitration NO_2 -derivatives of 2- and 4-halogenopyridines are not obtained. R. T.

2-Aminopyridine-5-sulphonamide and its derivatives. C. NAEGELI, W. KÜNDIG, and H. BRANDENBURGER (Helv. Chim. Acta, 1938, 21, 1746—1756).—2-Aminopyridine is transformed by $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ containing Al powder at 200—210° into 2-aminopyridine-5-sulphonic acid (I), m.p. 332—334°, in 60% yield. Its dry Na salt is converted by boiling Ac_2O into Na 2-acetamidopyridine-5-sulphonate [corresponding Cu salt, whence the free acid, m.p. 300—302° (decomp.)]. (I) and HNO_2 afford 2-pyridone-5-sulphonic acid (yield 92%), transformed by PCl_5 into 2-chloropyridine-5-sulphonyl chloride (II), m.p. 51°, also obtained from 1-methyl-2-pyridone-5-sulphonic acid and PCl_5 containing POCl_3 at 130—135°. Addition of (II) in COMe_2 to 20% NH_3 leads to 2-chloropyridine-5-sulphonamide (III), m.p. 158—159°, transformed by 20% NH_3 at 125—160° into 2-aminopyridine-5-sulphonamide (IV), m.p. 175—176.5° (Bz_2 derivative, m.p. 221—223°). (III) and 33% aq. NH_2Et at 100° or at 135—150° give 2-ethylaminopyridine-5-sulphonamide, m.p. 190—191° (yield 74%), or 5-sulphonethylamide, m.p. 139—141°, respectively. 2-Diethylamino-, m.p. 116—117°, 2-butylamino-, m.p. 121—122°, 2-allylamino-, m.p. 195—201°, 2-benzylamino-, m.p. 199—201°, and 2-anilino-, m.p. 181—183°, pyridine-5-sulphonamide are described. NH_2Ph and (II) in C_6H_6 afford 2-chloropyridine-5-sulphonanilide, m.p. 149—151°, converted by aq. NH_3 at 100—130° into 2-aminopyridine-5-sulphonanilide, m.p.

176—178°. (II) and $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{-NH}_2$ in $\text{C}_5\text{H}_5\text{N}$ at $\geq 40^\circ$ yield $p\text{-2'-chloropyridine-5'-sulphonamido-benzenesulphonamide}$, m.p. 200—202°, whence (25% NH_3 at 130—150°) $p\text{-2'-aminopyridine-5-sulphonamidobenzenesulphonamide}$, m.p. 200—202°. (II) and (IV) in anhyd. $\text{C}_5\text{H}_5\text{N}$ at $\geq 35^\circ$ afford $2\text{'-2'-chloropyridine-5'-sulphonamidopyridine-5-sulphonamide}$, m.p. 253—255°, decomp. 265°, whence aq. NH_3 (saturated at 0°) at 120—160° gives $2\text{'-2'-aminopyridine-5'-sulphonamidopyridine-5-sulphonamide}$, m.p. 260°. (III) and morpholine (V) at 120° give $2\text{'-N-morpholylpyridine-5-sulphonamide}$, m.p. 182—183°. Addition of H_2O to (II) and (V) in COMe_2 leads to $2\text{'-chloropyridine-5-sulphonmorphismolide}$, m.p. 143—144°. $2\text{'-N-Morpholylpyridine-5-sulphonmorphismolide}$ has m.p. 189—191°. All the compounds are well tolerated. H. W.

Sesqui-sodium salt of iodohydroxyquinoline-sulphonic acid. J. J. L. ZWIKKER and A. KRUYSSÉ (Pharm. Weekblad, 1938, 75, 1310—1315).—The prep. of a red Na salt, $\text{C}_9\text{H}_4\text{NI(ONa)·SO}_3\text{Na·C}_9\text{H}_4\text{NI(OH)·SO}_3\text{Na·10H}_2\text{O}$, is described. S. C.

[Synthesis of 1-alkylisoquinolines and polymethylenedi-1:1'-isoquinolines.] G. HAHN and H. F. GUDJONS (Ber., 1938, 71, [B], 2434).—An acknowledgement that the work of Child and Pyman (A., 1929, 1314) has been overlooked (cf. A., 1938, II, 513). H. W.

Nitrogen-terminated conjugated systems and maleic anhydride. F. BERGMANN (J. Amer. Chem. Soc., 1938, 60, 2811).—2-Styrylquinoline reacts with $(\text{CH}_2\text{CO})_2\text{O}$ in xylene at 100° , but the product absorbs H_2O from the air, yielding $2\text{'-styrylquinoline maleate}$, m.p. 165—167°, identified by conversion by CH_2N_2 into Me_3 dimethylpyrazoline-4:5-dicarboxylate, m.p. 103—105°. CHPh·CH·CO·NHPh reacts similarly, but the maleate formed decomposes spontaneously into CHPh·CH·CHO and $\text{cis-CO}_2\text{H·CH·CH·CO·NHPh}$, m.p. 210° (lit., 198°). R. S. C.

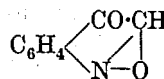
3-Arylquinoline-4-carboxylic acids. B. REICHERT and D. IVANOV (Arch. Pharm., 1938, 276, 515—520).—With isatin in hot 40% KOH methylphenylacetaldoximes, prepared by reduction of the β -nitrostyrenes, give 3-(methoxyaryl)quinoline-4-carboxylic acids, two of which have no significant antipyretic activity or toxicity. 3-3':4'-Methylenedioxyphenyl-, m.p. 268° (decomp.) (Et ester, m.p. 86°), 3-3':4'-, m.p. $239\text{--}5^\circ$ (decomp.) (Et ester, m.p. $118\text{--}119^\circ$), and 3-2':4'-dimethoxyphenyl-, m.p. $266\text{--}267^\circ$ (decomp.) (Me ester, m.p. 100°), 3-p-, m.p. 264° (decomp.), and 3-o-anisyl-, (I), m.p. 253° (decomp.), -quinoline-4-carboxylic acid are prepared. By heating the acids above the m.p. are obtained 3-3':4'-methylenedioxyphenyl-, m.p. 106° , and 3-p-anisyl-quinoline, m.p. 207° . With boiling HI ($d\ 1\text{'-7}$) (I) gives quinolino-3:4-4':3'-coumarin, m.p. $258\text{--}259^\circ$. R. S. C.

4-Arylamino-2-naphthylquinolines. K. DZIEWOŃSKI, (MLLE.) M. MARUSIŃKA, and J. MOSZEW (Bull. Acad. Polonaise, 1938, A, 331—342).—1:4- $\text{C}_{10}\text{H}_6\text{MeAc}$ (I) and CS(NHPh)_2 at 180° , then $220\text{--}280^\circ$, or $\text{CS(NH·C}_6\text{H}_4\text{Me·p)}_2$ at $180\text{--}230^\circ$ (270°), give 4-anilino-2-(4'-methyl-1'-naphthyl)quinoline (II), m.p. $214\text{--}215^\circ$ [hydrochloride, m.p. $240\text{--}241^\circ$ (decomp.)]; picrate, m.p. $285\text{--}286^\circ$; methiodide, m.p.

$291\text{--}292^\circ$; 4-N-NO-derivative, m.p. 165° (decomp.); 4-N-Ac derivative, m.p. 181° ; 4-N-Me derivative, m.p. 202° , and 4-p-toluidino-2-(4'-methyl-1'-naphthyl)-6-methylquinoline (III), m.p. 196° [hydrochloride, m.p. $316\text{--}317^\circ$; picrate, m.p. $271\text{--}273^\circ$; methiodide, m.p. $275\text{--}276^\circ$; 4-N-NO-, m.p. $233\text{--}235^\circ$ (decomp.); 4-N-Ac, m.p. $165\text{--}166^\circ$; 4-N-Me, m.p. $232\text{--}233^\circ$, derivative] respectively. 2:6- $\text{C}_{10}\text{H}_6\text{MeAc}$ and CS(NHPh)_2 at $180\text{--}210^\circ$, then 260° , give 4-anilino-2-(6'-methyl-2'-naphthyl)quinoline (IV), m.p. 172° (picrate, m.p. 278° ; 4-N-NO-derivative, m.p. 216° ; 4-N-Ac derivative, m.p. 197°), and $\beta\text{-C}_{10}\text{H}_7\text{·COEt}$ affords 4-anilino-2- β -naphthyl-3-methylquinoline (V), m.p. $178\text{--}179^\circ$ [hydrochloride, m.p. $253\text{--}254^\circ$; picrate, m.p. $261\text{--}262^\circ$; methiodide, m.p. $214\text{--}216^\circ$; 4-N-NO derivative, m.p. $153\text{--}154^\circ$ (decomp.); 4-N-Me derivative, m.p. $131\text{--}132^\circ$]. (II), (III), (IV), and (V), and KOH-EtOH under pressure at 200° , 210° , 215° , 200° respectively, for 4 hr., yield 4-hydroxy-2-(4'-methyl-1'-naphthyl)-, m.p. 240° , -2-(4'-methyl-1'-naphthyl)-6-methyl-, m.p. $271\text{--}272^\circ$, -2-(6'-methyl-2'-naphthyl)-, m.p. $318\text{--}319^\circ$, and -2- β -naphthyl-3-methyl-, m.p. $323\text{--}324^\circ$, -quinoline.

A. T. P.

Triangular structure for isatin. A. E. KLIJNHOUT (Chem. Weekblad, 1938, 35, 823—825).—The possibility of isatin having the annexed structure is discussed.



S. C.

Tautomerism and mesomerism of the carbamyl group and their relation to light absorption; o- and p-hydroxy-azo-compounds. F. ARNDT and B. EIRSTERT (Ber., 1938, 71, [B], 2040—2049).—In the tautomerism of compounds, R·CO·NHR' , it is clear that the relationships are more complicated than with keto-enol tautomerism, since any particular NH compound will have a structure intermediate between the mesomeric types R·CO·NHR' (I) and R·CO·NHR'^+ (II). Usually (I) will predominate, but when the C·N bond can form part of a conjugated or aromatic system (II) will be favoured; and as this has the same electron arrangement as the tautomeride R·C(OH)·NR' , optical measurements will not afford a distinction. In this way the results of Fromherz *et al.* (A., 1936, 1317; 1938, II, 381) and of Biltz (A., 1937, II, 78) with uric acid can be reconciled. The tautomerism of cyanuric acid, isatin, and of o- and p-hydroxy-azo compounds is discussed from the same aspect. F. J. G.

Synthesis of α -methylamino- β -3-indolylpropionic acid. E. J. MILLER and W. ROBSON (J.C.S., 1938, 1910—1912).—1-Methylhydantoin, indole-3-aldehyde, and $\text{C}_5\text{H}_{11}\text{N}$ give 5-(3'-indolyl)-1-methylhydantoin, m.p. $337\text{--}338^\circ$, which is reduced by H_2 in $\text{C}_5\text{H}_5\text{N}$ to 5-(3'-indolylmethyl)-1-methylhydantoin, hydrolysed [Ba(OH)_2 , 20 hr.] to α -methylamino- β -3-indolylpropionic acid, m.p. 245° (decomp.), in 90% yield. F. R. S.

Racemisation of amino-acids on acetylation with keten. R. W. JACKSON and W. M. CAHILL (J. Biol. Chem., 1938, 126, 37—41).—l-Tryptophan, l-phenylalanine, and abrine with limited amounts of keten in dil. NaOH yield optically active Ac deriv-

atives, but with enough keten to make the solution acid, complete racemisation occurs. With proline there is no racemisation in either case. A. LI.

Acridine. XIX. Absorption spectra of N-hydroxyacridone and its sodium salt. K. LEHMSTEDT and F. DOSTAL (Ber., 1938, 71, [B], 2432—2434).—Evidence is cited that the hydroxyacridone (I) obtained from $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$, C_6H_6 , and conc. H_2SO_4 is an equilibrium mixture $\text{C}_6\text{H}_4\text{<}\frac{\text{CO}}{\text{N(OH)}}\text{>C}_6\text{H}_4 \rightleftharpoons \text{C}_6\text{H}_4\text{<}\frac{\text{C(OH)}}{\text{NO}}\text{>C}_6\text{H}_4$ in which usually the equilibrium is displaced strongly towards the left. The observation of Tanasescu *et al.* (A., 1936, 1266, 1520) that (I) and its Na salt have closely similar absorption spectra could not be confirmed. H. W.

Hydantoins. LII. Synthesis of N-3-phenyl-5-p-hydroxybenzylhydantoin-N-1-acetic acid from tyrosine-N-acetic acid. (Miss) E. WARE (J. Amer. Chem. Soc., 1938, 60, 2653—2656; cf. A., 1933, 284).—Tyrosine-N-acetic acid (I) and PhNCO give 3-phenyl-5-p-hydroxybenzylhydantoin-1-acetic acid (II), m.p. 202—203°. The Me_2 ester, m.p. 84—85°, of (I), prepared by HCl-MeOH and liberated from its hydrochloride by the calc. amount of NaHCO_3 , with 25% HCl gives (II) (also obtained from Cu phenylureidotyrosine-N-acetate by H_2S) and with PhNCO gives Me_2 phenylureidotyrosine-N-acetate (III), $+\text{H}_2\text{O}$ and anhyd., m.p. 124—125° (decomp.). The Me ester, m.p. 140—141°, of (II) is prepared from (II) by HCl-MeOH or from (III) by hot H_2O or, better, 25% HCl . The structure of (II) is proved as follows. 5-p-Anisylidene-3-phenylhydantoin and $\text{CH}_2\text{Cl-CO}_2\text{Et}$ in NaOEt-EtOH give *Et* 5-p-anisylidene-3-phenylhydantoin-1-acetate, m.p. 89—91°, which with HI-red P yields (II) in one step. With conc. aq. Ba(OH)_2 at 100° (II) gives (I) and NH_2Ph . R. S. C.

Condensation of aminoantipyrene with aromatic amines in the presence of oxidising agents. E. EISENSTAEDT (J. Org. Chem., 1938, 3, 153—165).—Addition of 4 mols. of FeCl_3 to aminoantipyrene (I) (modified prep.) and the hydrochloride of an aromatic base having a $p\text{-H}$ gives dyes of type

$\text{NMe-CMe}_2\text{NPh-CO} \rightarrow \text{C:N:C}_6\text{H}_4\text{NR}_2\text{Cl}$, which are reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to colourless leuco-compounds. Thus, $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives the hydrochloride, "Antipyril Red B-3" (absorption max. at $4800 \pm 25 \text{ \AA.}$), reduced to 4-2':4'-diaminoanilinoantipyrene, m.p. 264-9—267-9° (hydrochloride, m.p. 258-6—259-1°), the latter product being also obtained by condensing (I) with 1:2:4- $\text{C}_6\text{H}_3\text{Cl(NO}_2)_2$ to 2':4'-dinitroanilinoantipyrene, m.p. 213-1—213-9°, and reducing this with Sn-HCl . NHPh_2 , (I), and $\text{K}_2\text{Cr}_2\text{O}_7$ in $\text{H}_2\text{SO}_4\text{-AcOH}$ give an impure dye, "Antipyril Blue A-93," reduced to 4-4'-antipyrildiphenylamine, m.p. 220-3—221-8°.

R. S. C.

Method of Garelli and Racciu for the preparation of piperazine. A criticism. D. B. ROLLINS and H. N. CALDERWOOD (J. Amer. Chem. Soc., 1938, 60, 2751—2752).—Contrary to Garelli *et al.* (Atti accad. Sci. Torino, 1934, 69, 162), $\text{NH}_2\text{[CH}_2\text{]}_2\text{OH}$ and H_2SO_4 or oleum give $\text{NH}_2\text{[CH}_2\text{]}_2\text{HSO}_4$. Piperazine gives a hexa- not a mono-hydrate. R. S. C.

Opening of the ring of the thiolactone of homocysteine. V. DU VIGNEAUD, W. I. PATTERSON, and M. HUNT (J. Biol. Chem., 1938, 126, 217—231; cf. A., 1936, 194).—*dl*-Homocysteine thiolactone hydrochloride (I) with aq. NaHCO_3 followed by aëration in presence of a trace of FeCl_3 yields an amorphous insol. compound, decomp. 260—270° (hydrolysed by conc. HCl to homocystine), but with NaHCO_3 in absence of air yields a mixture of *dl*- and *meso*-2:5-diketobis- β -thioethylpiperazine, m.p. 208° and 237°, respectively. The former is also produced by mixing the *d*- and *l*-compounds, m.p. 212°, $[\alpha]_D^{25} \pm 54^\circ$ in $\text{C}_5\text{H}_5\text{N}$ [prepared from the *d*- and *l*-forms, m.p. 194°, $[\alpha]_D^{25} \pm 21.5^\circ$ in H_2O , of (I)]. All four stereoisomerides are converted by CH_3PhCl and MgO in $\text{C}_5\text{H}_5\text{N}$ into the corresponding *S*-dibenzyl derivatives: *d*- and *l*-, m.p. 183°, $[\alpha]_D^{25} \pm 61.0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, *dl*-, m.p. 165°, and *meso*-, m.p. 176°. The *d*-dibenzyl compound was also prepared by treating *S*-benzyl-*d*-homocysteine with MeOH-HCl , then Ag_2O , and heating the product at 70° for 18 hr. *l*-Diketobis- β -thioethylpiperazine with H_2O_2 yields an amorphous product similar to the above. This and the amorphous product from the *d*-form of (I) with Na followed by CH_3PhCl , in liquid NH_3 , yield the *l*- and *d*-dibenzyl diketopiperazines. *dl*-*N*-Benzoylhomocysteine thiolactone, m.p. 134—136°, prepared by reducing ($\text{Sn} + \text{HCl}$) dibenzoylhomocystine, reverts to the latter with dil. NaOH , no amorphous compound being formed. It is concluded that such compounds are polymerides containing $\cdot\text{S}\cdot\text{S}\cdot$ linkings. All m.p. are corr. A. LI.

Structure of deoxyribonucleic acid. Diphosphoric esters of pyrimidine deoxyribosides. P. A. LEVENE (J. Biol. Chem., 1938, 126, 63—66; cf. A., 1938, II, 295).—Analysis of freshly prepared Ba diphosphothyminedeoxyriboside (A., 1921, i, 821) has been repeated, with the same result. A. LI.

4:5-Dihydroglyoxalines.—See B., 1938, 1391.

Catalytic hydrogenation of benziminazole derivatives. M. HARTMANN and L. PANIZZON (Helv. Chim. Acta, 1938, 21, 1692—1694).—Benziminazole is not hydrogenated under high pressure in presence of Ni at 200° or of Pt at 100° in various media. Its 2-alkyl derivatives are readily reduced (PtO_2 in AcOH) to the H_4 -compounds, 2-methyl-, (I), m.p. 224°, 2-ethyl-, m.p. 202°, and 2-cyclohexyl-, m.p. 267°, tetrahydrobenziminazole being thus obtained. 2-cyclohexylbenziminazole, m.p. 280°, is obtained by use of Ni at 180°. 1-Substituted benziminazoles cannot be hydrogenated in presence of Pt . The presence of a substituent in the C_6H_6 nucleus impedes hydrogenation even of the 2-substituted compounds as shown by the behaviour of 1-methyl-, 2:5-dimethyl-, and 1-ethyl-2:6-dimethyl-benziminazole. Hydrogenation of 5-ethoxy-2-methylbenziminazole causes loss of OEt and formation of (I). 1:2-Dimethyltetrahydrobenziminazole, b.p. 124°/4 mm., m.p. $\sim 43^\circ$ (picrate, m.p. 192°), is described. H. W.

Flavinduline derivatives. IX. K. YAMADA and N. HASEBE (J. Soc. Chem. Ind. Japan, 1938, 41, 290—292b; cf. A., 1938, II, 380).—The following halogen salts of flavinduline derivatives have been

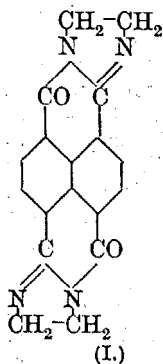
prepared from $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPr}^a$ and quinones: from phenanthraquinone: *chloride* ($+0.5\text{ZnCl}_2$), m.p. 195—197°, *bromide* ($+0.5\text{ZnCl}_2$), m.p. 204—206°, *iodide*, m.p. 159—161°; from 1:2-naphthoquinone: *chloride* ($+0.5\text{ZnCl}_2$), m.p. 190—192°, *bromide* ($+0.5\text{ZnCl}_2$), m.p. 199—201°, *iodide* ($+0.5\text{ZnCl}_2$), m.p. 163—165°; from o -benzoquinone: *chloride* ($+0.5\text{ZnCl}_2$), m.p. 217—219°, *bromide*, m.p. 229—231°, *iodide*, m.p. 140—142°. The colour reactions, solubility, dyeing properties, and fastness are described.

A. LI.

Complex compounds of rhenium.—See A., 1939, I, 36.

Preparation of naphthoyleneiminazolines.

H. E. FIERZ-DAVID and C. ROSSI (Helv. Chim. Acta, 1938, 21, 1466—1489).—The crude product of the oxidation of pyrene is suspended in H_2O , and treated with $(\text{CH}_2\cdot\text{NH}_2)_2$ followed by conc. HCl ; the resulting solution is made feebly alkaline with $2\text{N}\cdot\text{Na}_2\text{CO}_3$ and heated for a week at 80—81°, thus giving *naphthoylenedi-iminazoline* (I) [*picrate*, softens, without melting, at 250° (corr.)], which does not give a vat with alkaline $\text{Na}_2\text{S}_2\text{O}_4$. It is transformed by Br in $\text{C}_6\text{H}_5\text{Cl}_3$ at 180—200° into the compound, $\text{C}_{18}\text{H}_5\text{O}_2\text{N}_4\text{Br}_3$ or $\text{C}_{18}\text{H}_4\text{O}_2\text{N}_4\text{Br}_4$, which gives yellow-brown to brown shades on cotton from an alkaline vat. The following observations are incidental. Naphthalene-1:4:5:8-tetracarboxylic anhydride (II) and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ in boiling H_2O afford *naphthalene-1:4:5:8-tetracarboxydi-β-iminopropion-*



amide, with which the Hofmann degradation could not be effected satisfactorily. Analogously (II) and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ yield *Et*₂ *naphthalene-1:4:5:8-tetracarboxydi-β-iminopropionate*. *Et*₂ *naphthalene-1:4:5:8-tetracarboxydi-iminoacetate* has m.p. 304—305° (corr.). *Naphthalene-1:4:5:8-tetracarboxydi-iminoacetic acid* (III) is obtained by oxidising *naphthalene-1:4:5:8-tetracarboxydi-β-hydroxyethyl-di-imide* with $\text{K}_2\text{Cr}_2\text{O}_7$, AcOH , and $2\text{N}\cdot\text{H}_2\text{SO}_4$. With PCl_5 in $\text{C}_2\text{H}_2\text{Cl}_4$ followed by conc. aq. NH_3 (III) gives the corresponding *diamide*, also obtained directly from 1:4:5:8- $\text{C}_{10}\text{H}_4(\text{CO}_2\text{H})_4$ and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$. *Naphthalic anhydride* (IV) and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in boiling H_2O afford *naphthal-β-hydroxyethylimide*, m.p. 175—176° (corr.), transformed by conc. HI at 170—175° into *naphthal-β-iodoethylimide*, m.p. 226—227° (corr.). This with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$ in boiling PhNO_2 yields *naphthal-β-phthalimidoethylimide*, m.p. 237—238° (corr.), hydrolysed by 46% HBr at 170—180° to *naphthal-β-aminoethylimide*, m.p. 132° (Thiele), also obtained, with a substance $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_2$, m.p. 372° (corr.), from (IV) and $(\text{CH}_2\cdot\text{NH}_2)_2$. This [*picrate*, m.p. 280—281° (corr.) after softening at 270°; *Ac* derivative, m.p. 201—202° (corr.)] passes at 100° into *naphthoylene-2:3-iminazoline*, m.p. 184—185° (corr.) [*ethiodide*, m.p. 286—287° (corr.; decomp.), converted by prolonged warming with H_2O into the *base*, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, m.p. 92—93°; *picrate*, m.p. 294—295° (corr.; decomp.)].

Naphthal-β-chloroethylimide, m.p. 206—207° (corr.), and *β-bromoethylimide*, m.p. 222—223° (corr.), are described. *Naphthaliminoacetic acid*, m.p. 266—267° (corr.), obtained by oxidising the corresponding primary alcohol, gives a *Me* ester, m.p. 175—176° (corr.), and an *amide*, m.p. 323—324° (corr.; decomp.) after darkening at 306°, also obtained from (IV) and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ in boiling H_2O . These methods cannot be completely extended to (II), which with $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ in boiling H_2O yields *naphthalene-tetracarboxydi-β-hydroxyethyl-di-imide*, m.p. >360°. This is converted by conc. HBr at 170—180° into *naphthalene-1:4:5:8-tetracarboxydi-β-bromoethyl-di-imide*, m.p. 250—251°, by conc. HCl at 170—180° into the corresponding *chloride*, m.p. 288—289° (corr.) [also obtained by chlorination with PCl_5 in POCl_3], and by boiling conc. HI into the corresponding *iodide*, m.p. 293—294° (corr.). $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$ and $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 210—250° convert the iodide into *naphthalene-1:4:5:8-di-β-phthaliminoethyl-di-imide* [$(\text{NO}_2)_2$ -derivative]; $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ and KOH in boiling PhNO_2 transform it into the red compound, $\text{C}_{32}\text{H}_{28}\text{O}_8\text{N}_4\text{S}_2$, m.p. 260° (corr.) after softening at 215°.

H. W.

Phthalocyanines.—See B., 1938, 1394.

Catalytic properties of the phthalocyanines.—See A., 1939, I, 34.

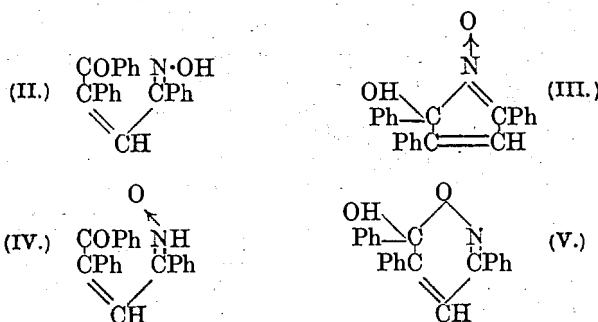
Action of nitric acid on ethyl α-phenacyl-acetoacetate. S. CUSMANO and (SIGNA.) G. MASSARA (Gazzetta, 1938, 68, 566—570).— HNO_3 (*d* 1.40) converts $\text{COPh}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ into *Et* 5-phenylisooxazole-3-carboxylate (I), converted by NH_2OH into 5-phenylisooxazole-3-carboxylhydroxamic acid, m.p. 177°, which with boiling 25% $\text{H}_2\text{SO}_4\text{-EtOH}$ yields the 3-carboxylic acid, m.p. 162° (decomp. to $\text{COPh}\cdot\text{CH}_2\cdot\text{CN}$), also obtained from (I) and aq. KOH-EtOH .

E. W. W.

Action of nitric acid on diphenacyl. S. CUSMANO and G. SIGILLÒ (Gazzetta, 1938, 68, 596—599).— $(\text{CH}_2\cdot\text{COPh})_2$ and HNO_3 (*d* 1.40) give 3-benzoyl-5-phenylisooxazole (A., 1938, II, 71, 162).

E. W. W.

Tautomerism of oximes. A. H. BLATT (J. Org. Chem., 1938, 3, 91—98).—Only one CO of *cis*- $\text{COPh}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COPh}$ (I) reacts with NH_2OH in acid or alkaline solution. The product is obtained as



oxime or as derivatives in four forms (II)—(V) (cf. A., 1934, 355; 1936, 733). The tautomerides opposite

in configuration to (II) and (IV) do not exist and are those which by ring-closure without inversion give (V) and (III), respectively. Prep. of 6-hydroxy-3:5:6-triphenyl- $\Delta^{2:4}$ -1:2-oxazine [-orthazine] (V), m.p. 159—160°, from (I) is detailed; it also sometimes gives some (?) β -amino- α,δ -triphenylbutane- α,δ -dione, m.p. 191—192°. With HCl-MeOH (V) gives the 6-OMe-compound (VI), m.p. 108°, proving its glucosidic nature, but the reaction is reversible, for longer treatment gives PhCN and COPh·CHPh·CH(OMe)₂ (VII); (VII) is a secondary product, derived from COPh·CPh·CH·OH, which (with PhCN) is obtained from (V) or (VI) by warm AcOH. With Ac₂O (V) gives the 6-acetate, m.p. 117—118°, converted by HCl-MeOH into (VI) and hydrolysed to (V) and EtOAc by NaOH-EtOH. PhSO₂Cl is without effect on (V), but PCl₅ causes mainly fission. (V) is insol. in aq., but sol. in alcoholic, alkali. MeI-NaOMe-MeOH with (V) gives a little (VI), but mainly the N-Me derivative, m.p. 167°, of (IV), hydrolysed by HCl to (I) and NHMe·OH. The production (Griffiths and Ingold, A., 1925, i, 1190) of 6-hydroxy-4:5-benz- $\Delta^{2:4}$ -1:2-oxazine and o -C₆H₄ $\begin{smallmatrix} \text{CH} \\ \text{CH(OH)} \end{smallmatrix} \rightleftharpoons \text{N} \rightarrow \text{O}$ from o -C₆H₄(CHO)₂ indicates that stereoisomeric oximes are formed in the reaction with NH₂OH.

R. S. C.

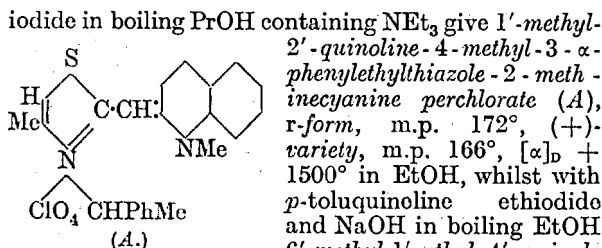
Iminazoles. VII. Iminazole compounds of the heterocyclic series. R. WEIDENHAGEN and U. WEEDEN (Ber., 1938, 71, [B], 2347—2360).—The formation of glyoxalines by the interaction of o -diamines, aldehydes, and Cu(OAc)₂ depends on the initial production of a Schiff's base which is subsequently oxidised. The reaction with heterocyclic o -diamines appears to occur with increasing difficulty when the two NH₂-groups and the hetero-atom are present in the same ring. 2:3-Diaminodiphenylene oxide, CH₂O, and Cu(OAc)₂ in aq. MeOH at 100° give 5':4'-iminazolo-2:3-diphenylene oxide, m.p. 217—218° [Cu salt; hydrochloride, decomp. 298°; picrate, m.p. 251° (decomp.)], converted by BzCl in anhyd. C₆H₅N into 1-benzoyliminazolo-5':4'-2:3-diphenylene oxide, m.p. 186—187°. The following iminazolo-5':4'-2:3-diphenylene oxides are obtained similarly by use of the requisite aldehyde: 2'-methyl-, m.p. 264.5° (Cu salt; hydrochloride, slow decomp. 278°; picrate, decomp. 279°); 2'-ethyl-, m.p. 274° (Cu salt; hydrochloride, decomp. 318°; picrate, m.p. 258°); 2'-isopropyl-, m.p. 234—235.5° (Cu salt; hydrochloride, decomp. 276°; picrate, decomp. 271°); 2'-hexyl-, m.p. 99—104° and, after re-solidification, m.p. 144° (Cu salt; hydrochloride, decomp. 281°; picrate, m.p. 215—216°); 2'-phenyl-, m.p. 247—247.5° (Cu salt; hydrochloride, m.p. 335—336°); 2'-p-nitrophenyl-, m.p. 363° (Cu salt; hydrochloride). 5:6-Diaminoquinoline is transformed by boiling HCO₂H or by CH₂O and Cu(OAc)₂ in aq. EtOH at 100° into iminazolo-4':5'-5:6-quinoline (+3H₂O), m.p. 216—217° (hydrochloride, decomp. 282—284°; 1'-Bz derivative, m.p. 166°). The following iminazolo-4':5'-5:6-quinolines are obtained by analogous methods: 2'-methyl-, (+1.5H₂O), m.p. (anhyd.) about 142° after becoming glassy at > 100° [Cu salt; hydrochloride, m.p. 313°; picrate, m.p. 269°]; 2'-ethyl-, (+2H₂O), m.p. 184° (Cu salt; hydrochloride, m.p. 284°); 2'-isopropyl-, (+1H₂O), softening

when anhydrous at 100—105° [Cu salt; hydrochloride, m.p. 316°]; 2'-phenyl-, m.p. 270° (also +1.5H₂O) (Cu salt; nitrate, decomp. 192°); 2'-p-nitrophenyl-, m.p. 356° (hydrochloride, m.p. 334.5°; Cu salt), obtained by oxidation of p-nitrobenzylidenediaminoquinoline, m.p. 222.5—223° (decomp.); 2'-styryl-, m.p. 258° [Cu salt; hydrochloride, m.p. 280° (decomp.)], from monocinnamylidenediaminoquinoline, m.p. 176—177°. 3:4-Diaminopyridine (I) is transformed by boiling HCO₂H into 4-amino-3(?)-formamidopyridine, m.p. 155.5—156°, and by boiling AcOH into 4-amino-3(?)-acetamidopyridine, m.p. 228—230°. CH₂O and Cu(OAc)₂ in boiling H₂O transform (I) into iminazolo-4':5'-3:4-pyridine, (+0.5H₂O), m.p. 170—171° [Cu salt; hydrochloride, m.p. 221° (decomp.)]. The following iminazolo-4':5'-3:4-pyridines are obtained similarly, heating in a sealed tube being sometimes necessary: 2'-methyl-, (+H₂O), m.p. 171° (Cu salt; hydrochloride, m.p. 271—273°); 2'-ethyl-, m.p. 191—192° [Cu salt; hydrochloride, m.p. 202° (decomp.)]; 2'-phenyl-, m.p. 224—225° (Cu salt; hydrochloride, m.p. 260°); 2'-p-anisyl-, m.p. 243° (Cu salt; hydrochloride, m.p. 254—255°); 2'-p-aminophenyl-, m.p. 324° (decomp.) (hydrochloride), by oxidation of mono-p-nitrobenzylidenediaminopyridine, decomp. 203°. H. W.

4:5-Dimethyl- and 4-methyl-5- β -chloroethylthiazole.—See B., 1938, 1391.

Properties of isosteric and structurally similar compounds. IX. Comparative investigations with 3-hydroxybenzthiazole. H. ERLÉNMEYER and H. UEBERWASSER (Helv. Chim. Acta, 1938, 21, 1695—1698; cf. A., 1938, II, 462).—Comparison of 3-hydroxybenzthiazole (I) with 8-hydroxyquinoline (II) shows that in the former the phenolic structure is more pronounced at the expense of the quinonoid form. (I) and (II) give mixed crystals. (I) is less useful than (II) in analytical chemistry. In the cases of Zn⁺⁺, Ni⁺⁺, and Cu⁺⁺ the insolubility of the ppts. with (I) renders them suitable analytically whereas with the Mg⁺⁺ and Al⁺⁺⁺ compounds this is not the case. The determination of (I) in these complexes is effected by bromination (KBr-KBrO₃-HCl) to 4:6-dibromo-3-hydroxybenzthiazole (III), m.p. 203°. (I), its Zn complex, and (III) fluoresce in ultra-violet light; among corresponding compounds only the Zn complex of (II) shows this behaviour. Qual. colour reactions with vanadates, molybdates, and tungstates are not given by (I). (III) in COMe₂ affords a very intense, green-black colour with Fe⁺⁺⁺. H. W.

Optically active cyanine dyes. J. GÖTZE (Ber., 1938, 73, [B], 2289—2291).—CHPhMe·NH₂ is converted by boiling AcOH-Ac₂O into acetphenylethylamide, r-form, m.p. 79° (+), m.p. 101—102°, [α]_D +150° in EtOH, and (—), m.p. 101—102°, [α]_D -170° in EtOH, varieties. Treatment of these with P₂S₅ followed by CH₂Cl·COMe and HClO₄ leads to 3- α -phenylethyl-2:4-dimethylthiazolium perchlorate, r-form, m.p. 172° (+), m.p. 162°, [α]_D +62° in EtOH, (—), m.p. 162°, [α]_D -68°, varieties; the corresponding chloride is transformed by KI into 3- α -phenylethyl-2:4-dimethylthiazolium tri-iodide, m.p. 92°. The requisite thiazolium perchlorate and 2-iodoquinoline meth-



ine-4-methyl-3- α -phenylethyl-2-thiazolemethinecyanine perchlorate, (—) form, m.p. 200°, $[\alpha]_D^{20} -1800^\circ$ in EtOH, is produced. The high $[\alpha]_D$ depends on the immediate neighbourhood of the asymmetric C to the main conjugation system.

H. W.

Preparation of tetramethylglucothiodiazolines.

M. H. WUYTS and F. VANDERVELDEN (Bull. Soc. chim. Belg., 1938, 47, 506—517; cf. A., 1933, 810; 1934, 537).—Tetramethylglucose and thiobenzoyl-phenylhydrazide in 5% EtOH-HCl yield tetramethylglucothiodiazoline, separated by EtOH into dextro- (I), $[\alpha]_{D_{405}}^{20} +1154^\circ$ in EtOH, and laevo- (II), $[\alpha]_{D_{405}}^{20} -905^\circ$ in EtOH, isomerides. In EtOH at 78°, (I) and (II) show rapid mutarotation to approx. the same α of $+100^\circ$ to 150° , which is followed by a slow rise in α to about 200°. The second slow change of α cannot be attributed to oxidation as is the case with the galactothiodiazolines (cf. A., 1936, 1275).

J. D. R.

Cyanine dyes; reaction of cyclic ammonium salts and indene. T. OGATA and S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 1197—1200; cf. A., 1934, 422; B., 1934, 314, 842).—2-(?-Phenylacetamido)vinyl-thiazoline- and -benzoxazole ethiodides, indene, and NEt_3 at 80° for 1 hr. afford 1:1'-diethyl-7:7'-o-phenyleneheptamethine-thiazolino-, m.p. 265° (decomp.), and 1:1'-diethyl-9:9'-o-phenyleneheptamethinebenzoxazolo-, m.p. 288° (decomp.), -cyanine iodides, respectively. Vals. for sensitising max. of the dyes are recorded.

A. T. P.

Hydrogenation of vitamin- B_1 and other quaternary thiazoles. F. LIPMANN and (Miss) G. PERLMANN (J. Amer. Chem. Soc., 1938, 60, 2574—2578).—Reduction of vitamin- B_1 (I), 4-methyl-5- β -hydroxyethylthiazole methiodide (II), nicotinamide ethiodide, 5-ethoxy-4-methylthiazole methiodide, Et 4-methylthiazole-5-carboxylate methiodide (III), m.p. 140°, and 4-methylthiazole-5-carboxylamide methiodide, cryst., by $\text{Na}_2\text{S}_2\text{O}_4$ in NaHCO_3 leads to absorption of 2 H and evolution of 3 CO_2 , but 4-amino-2-methyl-5-sulphomethylpyrimidino (IV) and 4-methyl-5- β -hydroxyethylthiazole (V) are unaffected. Reduction probably occurs at the 2:3-position of the quaternary thiazole ring. Benzthiazole methiodide (VI) is reduced by $\text{Na}_2\text{S}_2\text{O}_4$ - NaHCO_3 only if the methiodide has not been long in contact with the NaHCO_3 , which causes gradual decomp. to the non-reducible o- $\text{SNa}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CHO}$. The reduction products could not be purified or reoxidised, and that of (I) could not be oxidised to thiochrome and was biologically inactive. Since the Zn-HCl reduction product of (VI) is oxidised by I to (VI), it is probable that the initial $\text{Na}_2\text{S}_2\text{O}_4$ -products are similar, but are later irreversibly rearranged. The codehydrogenase action of (I) depends on a similar 2:3-reduction, and in this case

the primary reduction product is "fixed" as a compound with the protein. A colour appears temporarily during reduction, indicating the two-stage nature of the process. In presence of Pt-black (I) absorbs 2 H, (II) absorbs 4 H (1 mol. rapidly), (III) absorbs 2.4 H, (IV) absorbs 3.76 H (1 mol. rapidly) at p_H 8 (very little at p_H 10.5), (V) absorbs only a trace of H_2 , and 4-methylthiazole methiodide absorbs 3.6 H. 4-Methylthiazole-5-carboxylamide, cryst., is prepared from the ester by NH_3 -MeOH at 150°.

R. S. C.

Constitution of the antineuritic vitamin. K. MAKINO (J. Biochem. Japan, 1938, 28, 293—295).—Polemical on priority in the assignment of the Me group to its correct position in the pyrimidine nucleus (cf. Hörlein, A., 1938, II, 340).

F. O. H.

New general method for the conversion of amino-acids and polypeptides into alkaloids of the ephedrine and adrenaline types. P. P. T. SAH (Ber., 1938, 71, [B], 2300—2301).— $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{COCl}$ and alanine (I) yield N-carbobenzyl-oxy-dl-alanine, transformed by PCl_5 into an acid chloride, which with MgPhBr in anhyd. Et_2O or with C_6H_6 and AlCl_3 affords carbobenzyl-oxyaminopropiophenone, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMeBz}$. Catalytic reduction (Pd) of this affords PhMe, CO_2 , and phenyl- α -aminoethyl-carbinol, and a mixture of the optical isomerides of dl-norephedrine and dl-norisoephedrine. Cautious methylation transforms this into a mixture of dl-ephedrine and dl- ψ -ephedrine which is transformed into the hydrochlorides and extracted with CHCl_3 , thereby giving homogeneous dl-ephedrine hydrochloride. The free base is resolved by the optically active mandelic acids. Further, by use of glycine in place of (I) and of veratrole and AlCl_3 or *p*-bromoveratrole and Mg it is possible to obtain arterenol Me_2 ether, whence adrenaline. Tyrosine, tryptophan, histidine, thyroxine, carnosine, or glutathione may be used for the prep. of the Bergmann acid chloride.

H. W.

Proof of the synthesis and configurational relationships of abrine. W. M. CAHILL and R. W. JACKSON (J. Biol. Chem., 1938, 126, 29—36; cf. A., 1935, 1015).—Racemised abrine [from abrine and $\text{Ba}(\text{OH})_2$ in an autoclave] with NaOH and MeI-MeOH yields a betaine Me ester iodide, m.p. 194° (decomp.), and with keten in a solution kept alkaline to phenolphthalein yields an Ac derivative, m.p. 171°. These, and the picrate, are identical with the corresponding derivatives of synthetic α -methylamino- β -3-indolyl-propionic acid. Acetylabrina has m.p. 175—176°, $[\alpha]_D^{25} -148.4^\circ$ in 0.1N-NaOH. Betaines prepared from abrine and tryptophan have the same $[\alpha]$ as hypaphorine, showing that all three belong to the same configurational series.

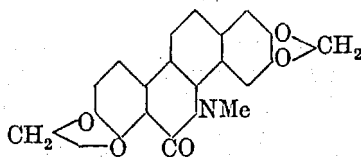
A. Lr.

Reducing properties of a tautomeric form of geneserine; a chain reaction. M. POLONOVSKI and P. DESGREZ (Compt. rend., 1938, 207, 685—687).—0.001N-Geneserine (I) in EtOH (1 c.c.) in vac. when insolated with a 300-watt lamp decolorises 0.6 c.c. of 0.001N-methylene-blue (II). In EtOH-AcOH at p_H 4.7, 0.48 c.c. of (II) is decolorised. The salts of (I) are less active than the base; the stronger is the acid the less is the activity. The nature of the solvent also changes the decolorising properties. The

N-oxido-grouping, which can exist in a tautomeric form, is the reactive one. Hydrasteine *N*-oxide and nornarceine *N*-oxide also give the reaction. (I) or dialkylhydroxylamines interfere with the determination of ascorbic acid with (II). (I) does not decolorise 2:6-dichlorophenol-indophenol in the light, but a trace of (II) will lead to decolorisation because the leuco-(II) serves to reduce the indophenol derivative.

J. L. D.

Alkaloids of *Sanguinaria canadensis*. F. SCHLEMMER and A. GEMPP (Arch. Pharm., 1938, 276, 506—515).—Isolation of *oxysanguinarine*, $C_{20}H_{13}O_5N$, m.p. 360—361° (vac.) (photomicrograph), probably having the structure shown, is described.

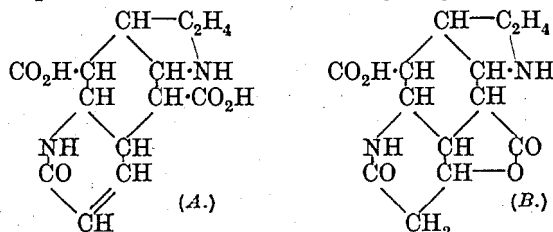


R. S. C.

Action of strychnine on Bordeaux B. D. B. DORT (Quart. J. Pharm., 1938, 11, 363).—The strychnine salt of 1-naphthaleneazo-2-naphthol-3:6-disulphonic acid is described.

P. G. M.

Strychnos alkaloids. CII. Isomeric substances $C_{13}H_{16}O_5N_2$ from brucinonic acid. H. LEUCHS (Ber., 1938, 71, [B], 2237—2238; cf. A., 1932, 953).—The NH_2 -acid is *A*. It is reduced (PtO_2 in H_2O) to the substance, $C_{13}H_{18}O_5N_2$, $[\alpha]_D^{20}$ -115.3°/d in 0.1*N*-HCl. It is not possible to isolate the product of its oxidation but hydrolysis shows it

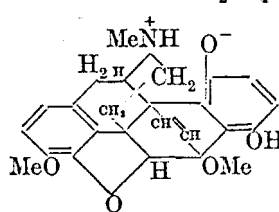


to be a derivative of $H_2C_2O_4$. The neutral reaction (CO_2H is neutralised by $\delta-NH$) and passive behaviour towards oxidation by MnO_4^- or catalytic hydrogen indicate that the lactone is *B*. The product of its hydrolysis readily loses H_2O with production of an unsaturated, isomeric acid.

H. W.

Thebaine-maleic anhydride, thebainequinone, thebainequinol, and the product, flavothebaone, of its isomerisation by acid. C. SCHÖPF, K. VON GOTTBERG, and W. PETRI (Annalen, 1938, 536, 216—257).—Thebaine (I) and maleic anhydride in boiling abs. C_6H_6 yield thebaine-maleic anhydride (II), m.p. 270° (decomp.), which gives a colourless solution in conc. H_2SO_4 . It is converted by KOH - $MeOH$ into the K_2 salt (III) of the corresponding dicarboxylic acid (*K H* salt). Hydrogenation (Pd - $BaSO_4$ or Pd - $PdCl_2$) of (II) could not be accomplished; with PtO_2 in $AcOH$ small amounts of substances sol. in alkali are obtained. Abs. $EtOH$ and HCl slowly transform (II) at room temp. into *Et*, thebainemaleate (IV), m.p. 152°, also obtained from (III) and EtI in $EtOH$ at 110° or by treatment of (II) with 20% HCl at 100° and subsequent esterification; the hydrochloride has

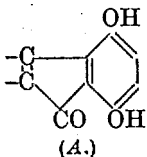
m.p. 248°. (III) could not be hydrogenated (PtO_2 in $EtOH$) and (II) does not absorb H (Pd - $CaCO_3$ in H_2O). Attempted demethylation by conc. HBr leads to non-uniform products. Freshly sublimed *p*-benzoquinone and (I) in boiling C_6H_6 yield thebainequinone, m.p. 250° (hydrochloride, m.p. 280° after becoming colourless). It is converted by $AcOH$ in boiling xylene or by KOH - $EtOH$ into thebainequinol (V), m.p. 270° [hydrochloride, decomp. 280°; *p*-toluenesulphonate (VI), m.p. 283° (decomp.)], which shows an intense blue-violet fluorescence in ultra-violet light and gives an orange-red solution in conc. H_2SO_4 . The presence of a double linking is established by its hydrogenation (PtO_2 in $AcOH$) to dihydrothebainequinol, m.p. 273°, which gives an almost colourless solution in conc. H_2SO_4 and is transformed by boiling



(V.)

HBr into the doubly demethylated product, $C_{23}H_{24}O_5NBr$, decomp. 295° (also dihydrate). (V) is converted by Ac_2O in C_5H_5N into a monoacetate, m.p. 259° (subsequent decomp.). With *p*- $C_6H_4MeSO_3Me$ at 120—130° (Me) gives (VI) and thebainequinol *Me* ether (VII), m.p. 238° [hydriodide, m.p. 261° (decomp.); *Ac* derivative, m.p. 259°] [hence the betaine structure of (V)]. In boiling $EtOH$ (VII) is transformed by $NaOEt$ and $NPhMe_3Cl$ into thebainequinol *Me*, ether (+ $EtOH$), m.p. 212°; (VI) could not be smoothly methylated by CH_3N_2 and is largely unchanged by *p*- $C_6H_4MeSO_3Me$ at 150°. (V) is readily converted by conc. HCl in $AcOH$ at 100° into *MeCl* and flavothebaone (VIII), $C_{24}H_{23}O_5N$ (+ $1H_2O$), m.p. 255—257°, or (+ $1MeOH$), m.p. 200—206° (softens 195°), normal hydrochloride monohydrate, decomp. 330° after slight softening at 285° and much softening and darkening at 312°; the *H* hydrochloride trihydrate, decomp. 312°, can be titrated with $NaOH$ without indicator, showing two end-points according to the scheme: $C_{24}H_{24}O_5NCl \cdot HCl \cdot 3H_2O + NaOH \rightarrow C_{24}H_{24}O_5NCl + NaCl + 4H_2O$ and $C_{24}H_{24}O_5NCl + NaOH \rightarrow C_{24}H_{23}O_5N + NaCl + H_2O$. (VIII) is an unsaturated ketone since it yields an oxime, m.p. 222° (decomp.) after softening at 206° [hydrochloride, m.p. > 350° after darkening at 260°; (?) *Ac*, derivative, m.p. 231°], which is converted by $SOCl_2$ into a base, m.p. 275° (decomp.) after slow softening at 258° [hydrochloride, becomes brown at 280°, black at 315°; *Ac*, derivative (+ $1PhMe$), m.p. 279° (decomp.)], and is reduced (H_2 - Pd - $BaSO_4$ in H_2O or $Na-Hg$ in $EtOH$) to dihydroflavothebaone, which is very readily autoxidised (hydrochloride, $C_{24}H_{26}O_5NCl \cdot 2H_2O$, m.p. 350° after softening at 340°, decomp. 365°, $[\alpha]_D^{25}$ +242° in abs. $MeOH$). The conjugation of the double linking with CO is established by the possibility of the use of $Na-Hg$ and by production of the compound, $C_{24}H_{24}O_5N_2 \cdot NH_2OH \cdot 0.5H_2O$, m.p. 282° (decomp.) (darkens at 265°), from (VIII) and NH_2OH in alkaline solution. The conversion of (VIII) by anhyd. $NaOAc$ and boiling Ac_2O or by Ac_2O - C_5H_5N at room temp. into triacetylflavothebaone, m.p. 273° after softening at 270°, and by $NPhMe_3OH$ into flavothebaone *Me*,

ether (IX), m.p. 253°, which is insol. in alkali, shows the presence of 3 phenolic OH groups, two of which are due to the quinol residue whilst the third is due to fission of the O bridge by HCl. N remains *tert.* in (VIII) as in (V) since (IX) cannot be acetylated and is quantitatively converted by Mel into the *methiodide*, m.p. 251°, transformed by boiling H₂O into the de-*base* C₂₈H₃₁O₅N, m.p. 160–161°, more conveniently obtained from *flavothebaone* Me₃ ether *methosulphate*, m.p. 288° (decomp.) (softens 270°); de-N-methylflavothebaone Me₃ ether *methiodide* has m.p. 295° (decomp.) (sinters 280°). The Me₁ and Me₂ ethers of (V) are similarly converted by conc. acid into *flavothebaone* Me₁ ether, m.p. 276° (decomp.) (softens 270°) [*hydrochloride dihydrate*, m.p. 308° (decomp.)], and Me₂ ether, m.p. 257° (softens 254°); both of these dissolve in alkali to a lemon-yellow solution and are further methylated by NPhMe₂OH to (IX). (IX) is hydrogenated (PtO₂ in AcOH) to *dihydroflavothebaone* Me₃ ether, m.p. 238° (turbid at 219–220°), [α]_D²⁵ +213° in CHCl₃ [*oxime*, m.p. 256–257° (softens 253°)], also obtained by means of Na–Hg. Br in AcOH at 80° transforms (IX) into *dibromo-flavothebaone* Me₃ ether, m.p. 270–272°, whereas bromination in AcOH or dil. AcOH containing NaOAc gives amorphous products of higher m.p. Oxidation of (IX) with BzO₂H in CHCl₃ or 33% H₂O₂ at 100° yields *flavothebaone* Me₃ ether N-oxide, m.p. 200–202° (decomp.) [*hydrochloride*, m.p. 312° (decomp.) (darkens at 250°)]. (IX) gives an *oxime*, m.p. 258° [*hydrochloride* (+2.5H₂O), m.p. 271–272° (decomp.) (softens 265°)], isomerised by SOCl₂ to the *isooxime* (+0.5MeOH), m.p. 212–213° [*hydrobromide*, C₂₇H₃₁O₅N₂Br, m.p. 275–276° (decomp.)]; this appears unchanged by KOH–MeOH but is converted by MeOH–HCl followed by HI into the *cryst. hydriodide*, C₂₈H₃₀O₅N₂I, m.p. 275–276° (decomp.). With EtOH–HCl and then with HBr a *hydrobromide*, m.p. 252–254°, is produced. Oxidation of (VIII) or (IX) generally yields amorphous, non-characteristic products. It is suggested that the arrangement A is produced during the formation of (VII).



Derivatives of dihydrothebainone.—See B., 1938, 1503.

Ergot alkaloids. XVI. Synthesis of substances related to lysergic acid. 6-Methyl-ergoline and ergoline-7-carboxylic acid. W. A. JACOBS and R. G. GOULD (J. Biol. Chem., 1938, 126, 67–76; cf. A., 1937, II, 434).—3'-Amino-5:6-benzoquinoline-7-carboxylic acid *lactam methiodide* (from the *lactam* and Mel at 100° for 18 hr.), m.p. 291–292° (decomp.), is reduced (PtO₂) to 3'-amino-1-methyl-2:3:4-trihydro-5:6-benzoquinoline-7-carboxylic acid *lactam*, m.p. 220–221°, further reduced (Na–BuOH) to 6-methylergoline, m.p. 210–212° (*hydrochloride*). 3-Amino-1-naphthoic acid sulphate with paraldehyde and HCl yields 5:6-benzoquinoline-7-carboxylic acid, m.p. 313–315° (decomp.) [*hydrochloride*, m.p. 314–316° (decomp.)]; Me ester, m.p. 114–116°; Et ester, m.p. 103–104°; Et ester *methiodide*, m.p. 201–203° (decomp.)], oxidised (SeO₂ in C₅H₅N) to 5:6-benzoquinoline-2:7-di-

carboxylic acid, m.p. 258° (decomp.), which with HNO₃ (d 1.58) at 0° yields the 3'-NO₂-compound, reduced [Fe(OH)₂–aq. NH₃] to the 3'-NH₂-compound *lactam*, m.p. 270–271° (decomp.) [NH₄ salt, m.p. 273–276° (decomp.)]; Me ester, m.p. 305–307°; Et ester, m.p. 275–277°. Partial hydrogenation (PtO₂) of this acid yields the 1:2:3:4-H₄-compound, m.p. 237–239° [Me ester (I), m.p. 234–236°; Et ester, m.p. 240–242°], whilst complete hydrogenation of its Et ester gives the 1:2:3:4:7:8:9:10-H₈-ester, m.p. 232–236°. Reduction (Na–BuOH) of (I), followed by careful decarboxylation, yields (?) *ergoline-7-carboxylic acid*. Ergoline purified by crystallisation of its hydrochloride has m.p. 201–203°.

A. LI.

Sulph-haemoglobin. H. O. MICHEL (J. Biol. Chem., 1938, 126, 323–348).—Haemoglobin (I) and the sulph-haemoglobin (II) which it yields with sol. inorg. sulphide and H₂O₂ (other oxidising agents are ineffective) do not differ in mol. wt., solubility, resistance to alkali, and cataphoretic mobility and the conversion is not accompanied by irreversible change in the haem of the haemoglobin. For the conversion 1 S is required for each Fe of (I). (II) contains 1 labile S not in form of free –SH. The reduced form of (II) is very stable but the oxidised form is unstable. At p_H between 6 and 8 the amount of (II) produced decreases as p_H increases. (II) combines with CO, the compound probably containing 1 CO for each Fe in reduced (II). Myohaemoglobin yields a myosulph-haemoglobin which combines with CO and is otherwise similar to (II). In presence of (I) H₂S is converted into H₂O₂ and S by O₂.

W. MCC.

Structure of protein molecules and their catalytic properties. D. L. TALMUD (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 153–157).—Treatment of *cryst. egg-albumin* in H₂O with aq. NH₂·CH₂·CO₂Et at 35° for 24 hr. and at room temp. for 48 hr., and determination of the pptd. diketopiperazine (I), shows that the protein retains much more of (I) than would be accounted for by adsorption. The results are quantitatively accounted for by the closed cyclol structure proposed by Wrinch, and indicate considerable “intraglobular” catalysis, the mechanism of which is discussed.

A. LI.

Arrangement of peptide chains in the molecules of sphaeroproteins. F. HAUROWITZ (Z. physiol. Chem., 1938, 256, 28–32; cf. A., 1936, 1462; Wrinch, A., 1938, I, 311).—The yields of OMe-compound obtained by treating ovalbumin (I) and oxyhaemoglobin with Me₂SO₄ and that of acetate obtained by boiling (I) with Ac₂O are < those required by the cyclol theory.

W. MCC.

Ultra-violet absorption spectrum of catalase. K. G. STERN and G. I. LAVIN (Science, 1938, 88, 263–264).—The ultra-violet absorption curve of horse-liver catalase shows a max. at ~2750 Å., due to the protein carrier of the enzyme, and a max. at 4050 Å., due primarily to the haemin residue. In contrast with other haemin-containing proteins such as haemoglobin, and chlorocruorin, the extinction coeff. at 2750 Å. is > that at 4050 Å. Visual examination of the spectrum shows a structure typical of a

globulin, and bands due to tryptophan, tyrosine, and phenylalanine appear to be present. L. S. T.

Changes of nitrogen content brought about by denaturation of proteins.—See A., 1939, III, 96.

Use of Trautz's micro-Dumas method [for determining nitrogen] with the apparatus of Pregl.—See A., 1939, I, 38.

Fine adjustment device for use with micro-Dumas apparatus. S. RANGASWAMI (Proc. Indian Acad. Sci., 1938, 8, A, 220—222).—A screw-regulated stopcock for controlling gas-flow is described.

A. Li.

Possible analytical uses of the apparatus of Grote and Krekeler and of that described in the DRP 642,166 of the I.G. Farbenindustrie in chemical technology, especially for the determination of halogens, sulphur, and other volatile elements. B. WURZSCHMITT and W. ZIMMERMANN (Z. anal. Chem., 1938, 114, 321—342).—The determination of S and halogens in org. substances is reviewed, and modifications of the Grote-Krekeler technique (B., 1934, 745) are described. A quick, explosive combustion, free from C-deposition, is obtained even with volatile org. compounds. The procedure is also applicable to the determination of Se and Hg, and of S in pyrites. L. S. T.

[Determination of selenium, mercury, halogen, and phosphorus.]—See A., 1939, I, 37.

Physical methods in the chemical laboratory. XXXVIII. Microscopic method of identifying organic substances. L. KOFER (Angew. Chem., 1938, 51, 703—707).—Identification of org. substances by the m.p. and n of the melt, determined microscopically, is described. The behaviour of 13 substances is described. R. S. C.

Reduction with hydriodic acid. Use in micro-determinations of hydroxyl groups. H. K. MITCHELL and R. J. WILLIAMS (J. Amer. Chem. Soc., 1938, 60, 2723—2726).—The reactions, $\text{ROH} + \text{HI} \rightarrow \text{RI} + \text{H}_2\text{O}$ and $\text{RI} + \text{HI} \rightarrow \text{HR} + \text{I}_2$, are applied at 100—134° on a micro-scale to determine alcohols. Only primary alcohols, polyalcohols, OH-acids, or negatively substituted compounds give useful results, reaction being incomplete or absent with other types. R. S. C.

Micro-chemical detection of *o*-diketo- and hydroxymethylene compounds. M. ISHIDATE (Mikrochim. Acta, 1938, 3, 283—290).—A drop of the test solution is treated with a drop of NH_2OH solution ($\text{NH}_2\text{OH} \cdot \text{HCl}$ 1 g., NaOAc 1 g., H_2O 2 c.c.), a drop of the resulting solution being put on filter-paper with a drop of 5% aq. $\text{Ni}(\text{OAc})_2$. A yellow or red colour is produced either immediately or after treatment with NH_3 vapour if an aliphatic $\cdot\text{CO}\cdot\text{CO}\cdot$ group is present. AcOH solution is used to ensure formation of all three isomeric oximes. The method can also be applied to detection of a $\cdot\text{CO}\cdot\text{CH}_2\cdot$ group if the CH_2 is first oxidised with SeO_2 . An EtOH solution of the sample is treated with a few particles of SeO_2 for 20 min. at 170° in a closed capillary tube, and the product is tested with NH_2OH and Ni^{++} . In detection of aromatic *o*-diketones, which yield no dioximes, a drop of the test solution is treated with 2

drops of a solution of 2 : 5 : 1- $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{NMe}_2)\cdot\text{OH}$, when a blue colour is obtained immediately or on keeping. The reagent is freshly prepared by suspending 0.05 g. of 2 : 5 : 1- $\text{NO}\cdot\text{C}_6\text{H}_3(\text{NMe}_2)\cdot\text{OH}$ in 5 c.c. of AcOH , shaking with Zn dust until decolorised, and then diluting to 10 c.c. with AcOH . J. W. S.

Micro-determination of formaldehyde. S. OHYAMA (Japan. J. Exp. Med., 1935, 13, 327—330).— CH_2O forms a ppt. with trypanflavine in presence of HCl . The method is sp. and sensitive.

CH. ABS. (e)

Micro-determination of lactic acid.—See A., 1939, III, 110.

Bromatometric determination of oxalate. L. SZEBELLÉDY and W. MADIS (Z. anal. Chem., 1938, 114, 347—350).—The oxalate solution is diluted to 30 c.c. and 0.5 g. of $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$, 0.5 g. of HgO , 20 c.c. of conc. H_2SO_4 , and 5 c.c. of glacial H_3PO_4 are added. The solution is titrated with 0.1N- KBrO_3 until a permanent bright pink colour is obtained. A comparison solution can be used with advantage. An intense violet colour, due to a Mn^{+++} salt, is formed during the titration. L. S. T.

Analytical separation of various classes of sugars. C. D. HURD and S. M. CANTOR (J. Amer. Chem. Soc., 1938, 60, 2677—2687).—Mixtures of (a) mono-, di-, and tri-saccharides or (b) hexoses and pentoses are analysed ($\pm 3\%$) by acetylation ($\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$) at 0°, followed by replacement of the acetal OAc by Cl using TiCl_4 , replacement of Cl by OMe by $\text{MeOH}\cdot\text{Ag}_2\text{CO}_3$, hydrolysis by $\text{NaOMe}\cdot\text{MeOH}$, methylation by $\text{Me}_2\text{SO}_4\cdot\text{NaOH}$, and fractional distillation. The procedures are not quant., but losses are about the same for each constituent (a correction is applied for mixtures of mono- and di-saccharides). Fructose is not amenable to this treatment. Other methods (e.g., direct methylation) failed. The glucose mother-liquors from the hydrolysate of maize starch are shown to contain mono- 55.2, di- 38.4, and tri-saccharides 6.4%. R. S. C.

Determination of maltose.—See A., 1939, III, 110.

Determination of pentosans.—See A., 1939, III, 110.

Bromatometric determination of thiocarbamide. L. SZEBELLÉDY and W. MADIS (Z. anal. Chem., 1938, 114, 253—256).—1 g. of KBr and 20 c.c. of conc. HCl are added to the neutral solution of $\text{CS}(\text{NH}_2)_2$ diluted to 35 c.c. After warming to 40—50°, 1 c.c. of 0.1% AuCl_3 is added, and the solution is titrated with 0.1N- KBrO_3 to the yellow colour obtained in a comparison solution of equal vol. containing 1 g. of KBr , 20 c.c. of conc. HCl , and 1 c.c. of 0.1% AuCl_3 . The determination is also suitable for micro-titrations with 0.1N- KBrO_3 when the above vols. and wt. of KBr are reduced to one tenth. The reaction is $3\text{CS}(\text{NH}_2)_2 + 4\text{HBrO}_3 + 3\text{H}_2\text{O} = 3\text{CO}(\text{NH}_2)_2 + 3\text{H}_2\text{SO}_4 + 4\text{HBr}$, and the KBr acts as a catalyst. L. S. T.

Ninhydrin reaction for determination of amino-acids. A. I. VIRTANEN and T. LAINE (Skand. Arch. Physiol., 1938, 80, 392—397, and Nature, 1938, 142, 754).—The reaction must be

carried out at p_H 2.0—2.2, since ninhydrin gives a distinct colour with $(NH_4)_2SO_4$ at p_H 2.5. The error is $\pm 5\%$ if the solution contains 2—12 mg. of NH_2-N per l. α -Alanine and leucine can thus be determined, giving $MeCHO$ and Bu^sCHO respectively. A. S.

Tyrosine determinations. C. REITER (Science, 1938, 88, 379).—Lugg's method (A., 1937, III, 447) is modified by making the 5 ml. of test solution N. with respect to H_2SO_4 . The buffering action of the NH_2 -acids present results in a p_H of ~ 1 . The mean val. found for the tyrosine (I) content of ovalbumin by this method then becomes 3.81%. By diluting the test solution to 25 ml., it can be kept for < 24 hr. before the colorimetric comparison without a fall in the (I) val. L. S. T.

Determination of carnosine and anserine.—See A., 1939, III, 26.

Titration of coloured solutions of sulphonic acids. I. N. KAMENSKI-SCHMIDT (Zavod. Lab., 1938, 7, 357—358).—Coloured solutions of sulphonation products cannot be titrated using the ordinary indicators. The solutions are decolorised by adding excess of $BaCl_2$, when the ppt. of $BaSO_4$ adsorbs coloured impurities, and the filtrate is titrated with 0.1N-NaOH (Me-orange), to give total acidity. A correction of 0.05 ml. should be added to the burette reading. R. T.

Determination of nitro-sulphonic acids, using zinc amalgam. M. M. LOBUNETZ (Bull. Sci. Univ. Kiev, 1937, 3, No. 3, 71—78).— m - $NO_2 \cdot C_6H_4 \cdot SO_3H$ is determined by reduction with Zn-Hg in 4N-HCl or H_2SO_4 , followed by titration of the resulting NH_2 -acid with standard $NaNO_2$ or $KBrO_3$ -KBr. The reduction method is also applicable to 1:5-, 1:6-, 1:7-, and 1:8- $NO_2 \cdot C_{10}H_6 \cdot SO_3H$, but titration of the resulting NH_2 -acids is rendered difficult by formation of intensely coloured solutions. R. T.

Microscopic identification of some important substituted naphthalenesulphonic acids. W. F. WHITMORE and A. I. GEBHART (Ind. Eng. Chem. [Anal.], 1938, 10, 654—661).—A method for the microscopic identification of several naphthylamine-, naphthol-, and aminonaphthol-sulphonic acids by means of their Bz derivatives is described. Characteristics and microscopic appearance of 15 acids and their derivatives are tabulated. F. N. W.

Determination of adrenalone in adrenalone hydrochloride. F. REIMERS (Dansk. Tidsskr. Farm., 1938, 12, 233—239).—Adrenalone hydrochloride (I) solutions may be titrated against 0.1N-NaOH (phenolphthalein) if the solution is conc. enough for the base to ppt. Vals. obtained are thus dependent on concn. (I) is best determined by pptg. the base from conc. aq. solution with $NaHCO_3$ at p_H 8; this is dissolved in 0.1N-HCl and back-titrated with 0.1N-NaOH to p_H 4.3 (bromophenol-blue). M. H. M. A.

Colorimetric determination of nicotinic acid and nicotinamide. H. KRINGSTAD and T. NAESS (Naturwiss., 1938, 26, 709; cf. Strafford *et al.*, B., 1933, 764).— C_5H_5N , nicotinic acid, nicotinamide, and

β -picoline are determined colorimetrically by means of CNBr and NH_2Ph in phosphate buffer at p_H 6.1.

A. Lr.

Determination of iodine in iodo-hydroxy-quinolinesulphonic acid. J. J. L. ZWIKKER and A. KRUYSSSE (Pharm. Weekblad, 1938, 75, 1305—1310).—The official Dutch method gives variable results according to the amount of tartaric acid used for removing excess of $KMnO_4$. The following simplified method is satisfactory. 120 mg. of iodo-hydroxyquinolinesulphonic acid are boiled for 30 min. with 100 c.c. of H_2O , 10 g. of $Na_2B_4O_7$, and 1 g. of $KMnO_4$. The hot solution is treated with 2 c.c. of EtOH, boiled for 5 min., and filtered, the residue being washed with saturated aq. Na_2SO_4 . The filtrate is treated with 10 c.c. of N-KI and 20 c.c. of 4N- H_2SO_4 and the liberated I titrated with 0.1N- $Na_2S_2O_3$. S. C.

Colour reactions of barbiturates. IV. Reaction of barbiturates with a polymethylene ring. M. PESEZ (J. Pharm. Chim., 1938, [viii], 28, 379—386).—*cyclo*Pentenylallylmalonylcarbamide (I) (1 mg.) with 5% vanillin-EtOH (5—6 drops) and H_2SO_4 - H_2O (2:1; 2 c.c.) rapidly gives an intense emerald-green colour, changed at 100° into a blue-green and then an intense blue. The coloured material is pptd. by H_2O (Et_2O and $CHCl_3$ extracts are yellow). The reaction is sp.; vanillin gives better results than analogous aldehydes. *cyclo*Hexenylethylmalonylcarbamide (II) when similarly treated gives a yellowish colour changed after 4—5 min. at 100° to reddish-violet. On dilution an intense red-violet colour is obtained (the coloured product is pptd.) ($CHCl_3$ and Et_2O extracts are cherry-red and yellow, respectively). PhOH with (I) and H_2SO_4 gives a golden-yellow colour at room temp. and an intense orange at 100°. Aq. NH_3 decolorises the solution through violet and blue. (II) when similarly treated gives a colourless solution at room temp., changing at 100° to an intense raspberry-red; H_2O changes this to violet and NH_3 decolorises it. (I) with vanillin and conc. HCl at 100° gives a dark blue colour, changed to blue-green with H_2O . The reaction is characteristic of (I). Resorcinol, (I), and conc. HCl at 100° give an intense red, changed to orange with H_2O , which with NH_3 gives a reddish-violet solution with a green fluorescence. (I), resorcinol, and H_2SO_4 at 100° give an orange colour changed to red with H_2O . $CHCl_3$ extracts a reddish-violet colouring matter. J. L. D.

Determination of the tryptophan content of casein. M. X. SULLIVAN, H. S. MILONE, and E. L. EVERITT (J. Biol. Chem., 1938, 125, 471—474).—To 99 c.c. of 17.5% HCl is added 1 c.c. of a 5% solution of p - $NMe_2 \cdot C_6H_4 \cdot CHO$ in 10% H_2SO_4 . After the addition of casein (1 g.), the mixture is heated at 85° for 15 min. and 0.3 c.c. of 0.3% H_2O_2 added. The well-shaken mixture is cooled to 20—25°, the vol. adjusted to 100 c.c. with H_2O , and the blue colour compared with appropriate standards. Various casein samples by this method and by the longer procedure of May and Rose as modified by Holm and Greenbank (A., 1923, ii, 666) were found to have a tryptophan content of 2.4%. W. O. K.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1939.

Photochemical autoxidation of iodoform.—See A., 1939, I, 89.

Hydrolysis of ethyl chloride by alkalis.—See A., 1939, I, 85.

Preparation of alkene and alkyne halides of high mol. wt. A. P. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1938, 5, 251—270).—Bu² oleate, b.p. 212—217°/7 mm., is reduced with Na in EtOH to Δ¹-octadecenyl alcohol (I), from which α-chloro- or α-bromo-Δ¹-octadecene are obtained (impure) in small yields by PCl₅ in Et₂O, in presence or absence of ZnCl₂, by PBr₃ in Et₂O in presence of C₅H₅N, or by SO₂Cl₂ in NPhMe₂ at 140°. HBr passed into a solution of Br in (I) at 110—135° yields α-bromo-Δ¹-octadecene, b.p. 192—194°/4 mm. R. T.

αβγδδ-Hexachlorobutane, principal end-product of the distillation of technical tetrachloroethane.—See B., 1939, 14.

Preparation of crotyl halides. R. VOIGT (J. pr. Chem., 1938, [ii], 151, 307—311).—Crotyl bromide (I), b.p. 101—104°, is obtained in 81.5% yield by passing butadiene through well-stirred 66% HBr at 30°. Crotyl iodide, b.p. 35°/12 mm., results similarly from 57% HI at 20° whereas crotyl chloride is prepared by means of HCl (*d* 1.19) containing FeCl₂, FeCl₃, HgCl₂, and HgCl at 0—10°. (I) obtained as above or from CHMe:CH:CH₂:OH gives the same dinitrobenzoate, m.p. 54°. H. W.

Photolysis of β-chloro-β-nitrosobutane.—See A., 1939, I, 89.

Epichlorohydrin and hydrogen sulphide.—See A., 1939, I, 86.

Pinacol-pinacolone rearrangement: preparation and rearrangement of tetramethylethylene bromohydrin. G. W. AYERS, jun. (J. Amer. Chem. Soc., 1938, 60, 2957—2960).—Whitmore's mechanism (A., 1932, 1016) of this rearrangement is supported by the following results. Anhyd. pinacol (I) (prep. from the hydrate by heating in vac.) and dry HBr—Et₂O give 21—27% of tetramethylethylene bromohydrin [β-bromo-βγ-dimethyl-*n*-butan-γ-ol] (II), m.p. 70.5°, volatile, lachrymatory. HBr—CHCl₃ and (I) at 0° give pinacol hydrobromide, [OH·CMe₂·CMe₂·OH₂⁺]Br[−], cryst., converted by moist air into (II). HBr and (I) in light petroleum (b.p. 30—50°) or CCl₄ give *d*-pinacol hydrobromide, (C₆H₁₄O₂)₂·HBr, m.p. 52—54°, also obtained as a by-product in Et₂O. Pinacolone is formed when (II) is heated in a closed tube at 100° or 150° or in air at 110° or when (II) is treated in Et₂O with aq. AgNO₃, Na₂S₂O₃, or Ag₂O.

R. S. C.

Electrolysis of magnesium chloride hexahydrate and -alcoholate in methyl and ethyl alcohol.—See A., 1939, I, 35.

Syntheses of terpenes from acetylene. A. E. FAVORSKI and A. I. LEBEDEV (J. Gen. Chem. Russ., 1938, 8, 879—883).—OH·CMe₂·CH:CH₂ and 20% H₂SO₄ (4—5 days at room temp.) yield a mixture of OH·CH₂·CH:CH·CMe₂, OH·CH₂·CMe₂·OH, linalool, and geraniol (traces). R. T.

Identification of methylisopropylcarbinol in Sharples [commercial] diethylcarbinol. F. A. KARNATZ and F. C. WHITMORE (J. Amer. Chem. Soc., 1938, 60, 3082).—Commercial CHEt₂·OH contains CHMePr²·OH, showing that rearrangement is not complete during hydrolysis of CHMePr²Cl, although it is complete when the chloride is prepared from the alcohol. R. S. C.

Resolution of *n*-propylallylcarbinol. R. CONSDEN, D. I. DUVEEN, and J. KENYON (J.C.S., 1938, 2104—2106).—*dl*-*n*-Propylallylcarbinol with *o*-C₆H₄(CO₂)O in C₅H₅N yields the *H* phthalate, m.p. 39—40°, which is resolved by its *brucine* salt, only the (−)-salt being obtained pure, m.p. 137—140° (decomp.), [α]_D²⁰ −22.0° in CHCl₃. This gives (−)-*n*-propylallylcarbinyl *H* phthalate, m.p. 39—40° ([α] for various λλ in EtOH, C₆H₆, C₅H₅N, CHCl₃, and CS₂ at room temp. are recorded), which is hydrolysed by NaOH to the (−)-*n*-propylallylcarbinol, b.p. 59—60°/20 mm. ([α] for various λλ alone at various temp. and in EtOH, C₆H₆, Et₂O, and CS₂ at room temp. are recorded) [benzoate, b.p. 147—148°/19 mm., α_D¹⁸ −5.85° (*l* = 0.5); acetate, b.p. 71°/23 mm., α_D¹⁹ −14.35° (*l* = 0.5)]. J. D. R.

Mechanism of replacement reactions in allyl compounds: reactions of (+)-*n*-propylpropenylcarbinol and its derivatives. C. L. ARCUS and J. KENYON (J.C.S., 1938, 1912—1920).—In replacement reactions of CHR:CH·CHR'X (A) which involve loss of optical activity the product may be CHR:CH·CHR'Y' (B) or CHRY·CH:CHR' (C), which cannot be distinguished if R = R' = Me. Replacement in (+)-*n*-propylpropenylcarbinyl *H* phthalate (I) (A; R = Me, R' = Pr²) is therefore studied. From the results, and those with (II) (below), and previous observations (A., 1938, II, 215, 231), it is concluded that the planar ion (CHMe·CH·CHPr²)[±] is formed, permitting entry at either C^α or C^γ. Possible mechanisms of inversion of configuration are discussed. With (I) and HCO₂H or BzOH, the *dl*-formate or -benzoate is obtained. With (I) (69% optically pure) and AcOH there is inversion of configuration, and a product of 0.2% max. rotation is

formed; when this is reduced it becomes inactive, and thus no asymmetry has been transmitted to C^γ (cf. C). Similarly (–)-Δ^β-δ-chloroheptene (II) (A; R = Me, R' = Pr^a, X = Cl), b.p. 44°/14 mm., α_D²⁵₄₆₁ –1.68°, obtained from the (+)-carbinol (III) and PCl₃ in C₅H₅N, and thus of opposite configuration to (III), with aq. Na₂CO₃ gives the carbinol, of 2% max. (+)-rotation. With MeOH–K₂CO₃, (II) from a carbinol of 30% optical purity gives the Me ether of 0.4% max. (+)-rotation. With AcOH–KOH, the dl-acetate is formed. All these are reduced to inactive products. Similarly dl-Δ^β-δ-chloroheptene (IV), b.p. 49°/21 mm., prepared from the dl-form of (III) yields inactive replacement products. When, catalytically, (IV) has absorbed 1H₂, the product contains residual (IV), some of the H₂ having attacked the C–Cl linking; reduction thus cannot be used to determine the optical purity of (II). The following are prepared: dl-n-propylpropenylcarbinyl p-nitrobenzoate, m.p. 40–41°, p-xenylurethane, m.p. 103.5°, formate, b.p. 53–54°/11 mm., and p-toluenesulphonate (V), decomp. 150°/0.1 mm., n_D²⁵ 1.5273. (+)-n-Propylpropenylcarbinyl p-toluenesulphonate (VI), α_D²⁵₄₆₁ +2.27°, is prepared from the (–)-carbinol. When (V) or (VI) is kept at 32°, a non-saponifiable product (sulphone?) is formed, α falling concurrently with ester content.

E. W. W.

Substituted acetylenes. XXIX. Preparation of acetylenic carbinols. K. N. CAMPBELL, (Miss) B. K. CAMPBELL, and L. T. EBY (J. Amer. Chem. Soc., 1938, 60, 2882–2884; cf. A., 1938, II, 388).—CH₃C:CM₂·OH, CH₃C:CM₂Et·OH (I), CH₃C:CM₂Pr^a·OH, CH₃C:CM₂(C₅H₁₁·n)·OH, 1-acetylenylcyclohexan-1-ol, CH₃C:CPhMe·OH, γ-phenyl-Δ^a-propinen-γ-ol, b.p. 114°/12 mm., γ-methyl-Δ^a-noninen-γ-ol, b.p. 96°/18 mm., Δ^a-noninen-γ-ol, b.p. 88°/40 mm., δ-methyl-Δ^a-decinen-δ-ol, b.p. 106°/20 mm., and δ-methyl-Δ^a-undecinen-δ-ol, b.p. 120°/19 mm., are obtained conveniently and in >50% yield from CH₃CNa or CR₃CNa and CORR' in liquid NH₃, while excess of the acetylene is passed into the solution (omission of this reduces the yield and more of the glycol is formed from C₂H₂). A reaction mechanism is postulated. Cone. HCl and (I) give 40% of β-chloro-β-methyl-Δ^a-butinene, b.p. 51–52°/135 mm.

R. S. C.

Production of butane-αγ-diol.—See B., 1939, 16.

Formation of βε-dimethyl-Δ^γ-hexine-βε-diol. A. T. BABAJAN (J. Gen. Chem. Russ., 1938, 8, 602–607).—The following mechanism is proposed for Kazarian's reaction (A., 1935, 729): C₂OMe₂ + KOH → OH·CMe₂·OK $\xrightarrow{+CaO_2}$ (OK·CMe₂·C₂)₂ + Ca(OH)₂.

R. T.

Photochemical reactions in the o-nitrobenzylidenacetate series. XII. Mono- and di-o-nitrobenzylidenepentaerythritol, tri-o-nitrobenzylidenedulcitol, and di-o-nitrobenzylideneadonitol. I. TANASESCU and I. ILIESCU (Bull. Soc. chim., 1938, [v], 5, 1446–1457; cf. A., 1933, 275; 1936, 1234).—Extraction of o-nitrosobenzoyl-o-nitrobenzylidenepentaerythritol, m.p. 135° (I) (obtained by insolation of di-o-nitrobenzylidenepentaerythritol), with cold Et₂O gives a more labile isomeride, m.p. 85–90° (II) (formulae discussed), which when slowly heated passes

into (I). With BzCl–C₅H₅N, (I) and (II) give the same Bz derivative, m.p. 83–84°, and with HCl–EtOH–H₂O afford the same o-nitrobenzylidenepentaerythritol (III), m.p. 144–145° (dibenzoate, m.p. 111°). (I) and NH₂Ph–EtOH for 1 hr. form a monoazo-derivative, C₂₅H₂₃O₇N₃, m.p. 110° (previous shrinking), thus proving the presence of 1 NO only. (III) and p-NO₂·C₆H₄·CHO (excess) with H₂SO₄ or P₂O₅ give di-p-nitrobenzylidenepentaerythritol, m.p. 234–235°. Insolation of (III) in CHCl₃ gives o-nitrosobenzoylpentaerythritol, m.p. 95° (? 105°) (tribenzoate, m.p. 86–88°). Dulcitol and o-NO₂·C₆H₄·CHO–P₂O₅ at 50° for 4–5 hr. give tri-o-nitrobenzylidenedulcitol, m.p. 92–94°, converted (in CHCl₃) by light into βε-di-o-nitrosobenzoyl-γδ-o-nitrobenzylidenedulcitol, m.p. 138–140° (αξ-dibenzoate, m.p. 125°; αξ-dibenzene-sulphonate, m.p. 116°). Adonitol and o-NO₂·C₆H₄·CHO in H₂SO₄ (1:1) give αξδε-di-o-nitrobenzylideneadonitol, m.p. 183–185°, insolated (CHCl₃) to δ-o-nitrosobenzoyl-αβ-o-nitrobenzylideneadonitol, m.p. 100° [γδ-dibenzoate, m.p. 104° (previous shrinking); γδ-dibenzene-sulphonate, m.p. 87°; NH₂Ph–EtOH gives the monoazo-compound, C₂₅H₂₃O₈N₃, m.p. 175°].

A. T. P.

Synthesis of r-arabitol and adonitol. R. LESPIEAU (Bull. Soc. chim., 1938, [v], 5, 1638–1641).—Mainly a detailed account of work already reported (A., 1936, 1229; 1938, II, 346).

CH₃C:[CH·OAc]₂·CH₂·OAc is obtained from CH₃C:[CH·OH]₂·CH₂Cl. CH(CH₃CH₂)₂·OH with AgClO₄ and a little OsO₄ gives a syrup, acetylation of which yields some r-arabitol penta-acetate. R. S. C.

Explosions and other dangers in using ether, and their prevention. J. STAMM (Chem. Ztg., 1939, 63, 11–13).—Published work on the explosion of mixtures containing Et₂O and its auto-oxidation products, the purification of Et₂O, and tests for its purity, especially with reference to H₂O₂, are reviewed.

C. R. H.

Isomerisation of dimethylvinylethylene oxide into αα-dimethyl-Δ^β-butenal. Migration of vinyl. Y. DEUX (Compt. rend., 1938, 207, 920–921).—Mesityl oxide with Al₂(OPr^a)₃ affords CMe₂·CH·CHMe·OH which when distilled over H₂SO₄ (pumice) gives dimethylvinylethylene, b.p. 75–76°/760 mm., converted into a chlorohydrin, which with K in dry Et₂O gives dimethylvinylethylene oxide (I), b.p. 80–81°/60 mm. When (I) is passed over fuller's earth at 250°, or when it is treated with MgBr₂·Et₂O, it affords αα-dimethyl-Δ^β-butenal, b.p. 87–88°/70 mm., reduced to ββ-dimethylbutyl alcohol, b.p. 135–137°/760 mm. (Ph carbamate, m.p. 63–64°) [identical with the alcohol obtained by interaction of CMe₂Et·MgCl (II) and HCO₂Et], oxidised to αα-dimethylbutyric acid, b.p. 113–114°/53 mm. (amide, m.p. 102–103°; anilide, m.p. 92–93°), identical with the acid prepared from (II) and CO₂.

J. L. D.

Methylene dinitrate. G. TRAVAGLI (Gazzetta, 1938, 68, 718–721).—(CH₂O)₃ and HNO₃ (d 1.52) in H₂SO₄ at 3–5° give methylene dinitrate (I), CH₂(O·NO₂)₂, b.p. 75–77°/20 mm., hydrolysed by KOH to KNO₂, KNO₃, CH₂O, and some HCO₂H and MeOH. In the products from C₂H₄ and HNO₃ (I) is not detected.

E. W. W.

Acid catalysis in liquid ammonia. III. Effect of α -substituents on the ammonolysis of esters. L. F. AUDRIETH and J. KLEINBERG (J. Org. Chem., 1938, 3, 312—316; cf. A., 1938, I, 258).—Conversion of esters into amides by liquid NH_3 is shown to be always (8 examples) very greatly accelerated by NH_4Cl , in accordance with the view that NH_4Cl acts as an acid in NH_3 . The effect of R in $\text{CH}_2\text{R}\cdot\text{CO}_2\text{Et}$ is shown by the following relative reaction rates: $\text{CN} > \text{CO}\cdot\text{NH}_2 > \text{CO}_2\text{Et} > \text{OEt} > \text{Ph} > \text{H}$; the rates for $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et} > \text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ are intermediate between those of $\text{CH}_2(\text{CO}_2\text{Et})_2$ and $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$. Prep. of $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{NH}_2$ and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{NH}_2$ in 80.5 and 74—76% yield, respectively, is described. R. S. C.

β -Alkoxyethyl esters of chlorocarbonic and carbamic acids. H. G. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1938, 60, 2933—2934).—The appropriate alkoxyethyl chloroformate (prep. by COCl_2 at $<0^\circ$) with aq. NH_3 gives β -methoxy-, m.p. 46.8° , -ethoxy-, m.p. 62.2° , -n-, b.p. 132.2 — $132.5^\circ/7$ mm., and -iso-propoxy-, m.p. 53° , -n-, b.p. 132.2 — $132.4^\circ/2.5$ mm., -iso-, b.p. 133 — $134^\circ/5$ mm., and -sec-butoxy-, b.p. $135.4^\circ/3$ mm., -n-, b.p. $142.2^\circ/3$ mm., and -iso-amyl-oxy-, b.p. $131.4^\circ/1.5$ mm., - β' -methyl-n-butoxy-, b.p. 129 — $130^\circ/2$ mm., - α' -ethyl-n-propoxy-, b.p. 133 — $134^\circ/2.5$ mm., and - α' -methyl-n-butoxy-ethyl carbamate, b.p. 137 — $138^\circ/3.5$ mm. Urethane is more active and less toxic than the OEt esters, equal to the Pr esters, but less active and less toxic than the Bu and $\text{O}\cdot\text{C}_6\text{H}_{11}$ esters. β -n-Propoxy-, b.p. $78.3^\circ/13$ mm., β -n-butoxy-, b.p. 93 — $93.5^\circ/14$ mm., and β -n-amyl-oxy-ethyl chloroformate, b.p. $104.3^\circ/12$ mm., are described. B.p., n_D^{25} , d_4^{25} , and γ^{25} are given for all the chloroformates. R. S. C.

Neutral and basic lead monochloroacetates. E. GRILLOT (Compt. rend., 1938, 207, 996—998; cf. A., 1935, 1089; 1937, II, 440).— $(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Pb}$ (I) when boiled with H_2O or n-aq. NH_3 affords a basic salt (II), $(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Pb}\cdot\text{PbO}$, together with small but variable amounts of $(\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Pb}\cdot\text{PbO}$. (II) dissolves easily in hot aq. (I) to give $[(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_3\text{Pb}_2]\text{OH}$, which has a strongly alkaline reaction. J. L. D.

Uranyl salts of substituted organic acids. J. H. KŘEPELKA and Z. RĚSŮ (Coll. Czech. Chem. Comm., 1938, 11, 559—581).—The prep. and properties of the following UO_2 salts are described: α -chloro-, β -chloro-, α -bromo-, β -bromo-, β -iodo-propionate, dibromosuccinate, thiolacetate, α -thiolpropionate, o-chlorobenzoate (I). The salts decompose slowly in daylight and more rapidly in ultra-violet light; decomp. being catalysed by Et_2O . The aliphatic salts, of which the β -compounds are more stable, give CO_2 , basic salts, and U_3O_8 in ultra-violet light; in daylight more U_3O_8 and less of the basic salts are obtained, and CO_2 is evolved only near the end of the decomp. (I), the most stable salt prepared, gives UO_2 salicylate and HCl in ultra-violet light. F. H.

Action of sodium ethoxide on γ -halogenocrotonic esters. R. RAMBAUD (Bull. Soc. chim., 1938, [v], 5, 1552—1564; cf. A., 1935, 1105).— $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ (I) and $\text{NaOEt}\cdot\text{EtOH}$ at 50° give Et γ -chloro- β -ethoxybutyrate (II), b.p. 108 —

$108.3^\circ/20$ mm. From $\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, the analogous γ -Br-compound (III), b.p. 112 — $114^\circ/15$ mm., can be isolated, but usually there is loss of HBr, probably through (III), with formation of Et 2-ethoxycyclopropanecarboxylate (IV), b.p. 74 — $75.5^\circ/13$ mm., also obtained from (II) by distillation with dry KOH [some succinic acid (V) is also formed] or from (I) and NaOEt in very low yield, or from (III) and NaOEt. (IV) and CrO_3 or H_2O_2 give traces of (V); (IV) and NaOH in a sealed tube give 2-ethoxycyclopropane-1-carboxylic acid, b.p. $122^\circ/14$ mm., converted by CrO_3 , or more slowly by air, into (V). The mechanism of formation of (IV) is discussed. $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ distilled with dry KOH gives cyclopropanecarboxylic acid and its Et ester. A. T. P.

Diene syntheses with derivatives of sorbic acid. T. WAGNER-JAUREGG and E. HELMERT (Ber., 1938, 71, [B], 2535—2543).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and sorbyl chloride (I) at 0° and subsequently at 110° afford β -chloroethyl sorbate, b.p. $115^\circ/15$ mm., converted by NHEt_2 at 100 — 120° into β -diethylaminoethyl sorbate, b.p. $109^\circ/0.45$ mm. (hydrochloride), also obtained from sorbic acid (II), $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ (III) and HCl at 100° or from (I) and (III). (II) and (III) when heated in N_2 at 200° afford mainly a product, $\text{C}_{12}\text{H}_{21}\text{O}_2\text{N}$, b.p. 190 — $200^\circ/0.15$ mm. Acrylyl chloride and (I) in boiling xylene give 4-methyl- Δ^5 -tetrahydroisophthalyl chloride (IV), b.p. 118 — $122^\circ/0.3$ mm., hydrolysed to the corresponding acid, m.p. 282.5 — 283° , which is dehydrogenated by Br at 150° to 4-methylisophthalic acid (V), m.p. 330 — 331° (corr.). (IV) is converted by NHEt_2 at 0° and then at 40° into 4-methyl- Δ^5 -tetrahydroisophthalbisdiethylamide, b.p. 190 — $194^\circ/0.2$ mm. 4-Methylisophthalbisdiethylamide has b.p. 200 — $203^\circ/0.1$ mm., m.p. 74 — 74.5° (corr.). 3-Carb- β -chloroethoxy-6-methyl- Δ^4 -cyclohexene-1-carboxyl chloride, b.p. 150 — $154^\circ/2$ mm. [degraded by Br to (V)], is converted by NHEt_2 at 110° into 3-carb- β -diethylaminoethoxy-6-methyl- Δ^4 -cyclohexene-1-carboxyldiethylamide, b.p. $198^\circ/0.3$ mm. Maleic anhydride and $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5\text{Cl}$ give 3-carb- β -chloroethoxy-6-methyl- Δ^4 -tetrahydrophthalic anhydride, m.p. 124° (corr.), degraded by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution to $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ and dehydrogenated and hydrolysed by Br to 3-carboxy-6-methylphthalic anhydride, m.p. 180° . Similarly with $(\text{C}\cdot\text{CO}_2\text{Me})_2\text{Me}_2$ 3-carb- β -chloroethoxy-6-methyl-3:6-dihydrophthalate, b.p. 190 — $194^\circ/0.25$ mm. (slight decomp.), is produced. H. W.

Relative stability of aromatic and aliphatic monoglycerides. B. F. DAUBERT and C. G. KING (J. Amer. Chem. Soc., 1938, 60, 3003—3004).—Glyceryl β -p-bromobenzoate (I), m.p. 95.2° , and β -palmitate (II) are rapidly converted into the α -esters by $0.1\text{N}\cdot\text{HCl}$ or NH_3 in EtOH, but for (II) $0.0067\text{N}\cdot\text{HCl}$ or $0.0125\text{N}\cdot\text{NH}_3$ is as effective as is $0.05\text{N}\cdot\text{HCl}$ or $0.067\text{N}\cdot\text{NH}_3$ for (I). No shift occurs with (I) or (II) at 7° above the m.p. R. S. C.

Transformations of stearic acid in the solid state.—See A., 1939, I, 13.

Intermolecular oxidation of oleic acid. M. BRAMBILLA (Annali Chim. Appl., 1938, 28, 444—454).—Oleic acid, heated to 325° in N_2 , yields CO_2 , octoic

and sebacic acid, and an unsaponifiable residue which, on fractionation, affords C_8H_{16} and $C_{10}H_{20}$ on distillation at normal pressures and $C_{16}H_{32}$ at 20 mm. The mechanism of the degradation is discussed.

F. O. H.

Lipins of tubercle bacilli. LIV. Mycolic acid. F. H. STODOLA, A. LESUK, and R. J. ANDERSON. **LV. Wax fractions of human tubercle bacillus.** C. W. WIEGHARD and R. J. ANDERSON. **LVI. Wax of the bovine tubercle bacillus.** J. CASON and R. J. ANDERSON (J. Biol. Chem., 1938, 126, 505—513, 515—526, 527—541).—**LIV** (cf. A., 1936, 1028). Hydrolysis of the "unsaponifiable wax" of human tubercle bacilli with C_6H_6 -MeOH-KOH for 80 hr. removes traces of fatty acids and phthiocerol, leaving *mycolic acid*, $C_{86}H_{167}(OH)(OMe)_{0.6}CO_2H$, m.p. 54—56° (corr.), $[\alpha]_D^{25} + 1.8^\circ$ in $CHCl_3$ [*Me ester* (CH_2N_2), m.p. 43—45°], a saturated acid which with HI and PhOH gives I-acids of varying composition, and when heated at 280—350°/0.5 mm. yields *n*-hexacosic acid and a non-acidic residue.

LV (cf. A., 1936, 899). The wax-like material from EtOH-Et₂O extracts of the bacilli, insol. in cold COMe₂, has been separated into three fractions by pptn. from EtOAc by cooling, and by addition of COMe₂. The least sol. fraction when hydrolysed (C_6H_6 -MeOH-KOH) yielded H₂O-sol. substances, glycerol (I), mannose, and inositol, phthiocerol (II), and acids which were separated by pptn. from EtOH with Pb(OAc)₂: palmitic, stearic, *n*-hexacosic (III), tuberculostearic, mycolic, and an acid, $C_{31}H_{62}O_2$ (?), m.p. 37—38°, $[\alpha]_D^{25} - 10.4^\circ$ in Et₂O. The more sol. fractions contained (I), carbohydrates, (II), fatty acids, phthioic acid, unsaturated acids hydrogenated to (III), and acids similar to mycolic but of lower mol. wt.

LVI. The $CHCl_3$ -sol. wax from bovine tubercle bacilli, purified by repeated pptn. from Et₂O by MeOH, has been hydrolysed (EtOH-KOH) and the products separated into four fractions: (a) H₂O-sol. substances, (I), glycerylphosphoric acid, a disaccharide monophosphoric acid giving a positive Scherer test for inositol, and a neutral polysaccharide containing N, hydrolysed (dil. H₂SO₄) to inositol monophosphoric acid, mannose, inositol, and another reducing sugar; (b) Et₂O-EtOH-insol. acids containing OH and OMe groups, of mean mol. wt. 1200, including bovine mycolic acid, m.p. 56—58°, $[\alpha]_D + 2.7^\circ$ in $CHCl_3$, which when heated at 250—300° under reduced pressure yields (III); (c) Et₂O-EtOH-sol. acids, palmitic, an inactive branched-chain (?) acid, $C_{24}H_{48}O_2$, m.p. 76—77° (*Me ester*, m.p. 39—42°), an inactive branched-chain acid, $C_{18}H_{36}O_2$, m.p. 29—30° (*Me ester*, b.p. 112—114°/0.006 mm.; 2:4:6-tribromoanilide, m.p. 96—96.5°), unsaturated acids, and a mixture of saturated *l*-acids of mean mol. wt. 430; and (d) neutral substances, (II), and an unknown non-cryst. substance

A. LI.

Condensation of formaldehyde with α -methylacetacetic ester. J. BURKHARD (Bull. Soc. chim., 1938, [v], 5, 1664—1669).— $CHMeAcCO_2Et$, CH_2O (1.5 mols.), and a little aq. K_2CO_3 at -10° give *Et α -methyl- α -hydroxymethylacetacetate*, b.p. 96° (slight decomp.)/1.5 mm. (*acetate*, b.p. 94—96°/0.2 mm.; *oxime*, m.p. 165°; does not react with PhNCO),

which decomposes slowly at 80° and rapidly at 140° or when distilled at 14 mm.

R. S. C.

Potentiometric titration of complex compounds with several oxidisable components.—See A., 1939, I, 103.

Introduction of substituted vinyl groups. II. (1-Methylpropenyl)alkylmalonic esters. III. (Dialkylvinyl)alkylcyanoacetic esters. A. C. CORE and (Miss) E. M. HANCOCK (J. Amer. Chem. Soc., 1938, 60, 2901—2902, 2903—2906; cf. A., 1939, II, 5).—**II.** *Et α -carbethoxy- γ -methyl- Δ^{β} -pentenoate* [*Et₂ α -methylpropylidenemalonate*] [prep. from $CH_2(CO_2Et)_2$, COMeEt, and $ZnCl_2$ in Ac_2O at 110°, b.p. 119—120°/9 mm., with $NaNH_2$ or, less well, $NaOEt-EtOH$, followed by $RHAl$ or R_2SO_4 , gives good yields of *Et₂ methyl-*, b.p. 126—127°/15 mm., *ethyl-*, b.p. 124—124.5°/9 mm., *propyl-*, b.p. 128—131°/9 mm., *allyl-*, b.p. 124—129°/9 mm., and *butyl-*, b.p. 159—160°/22 mm., *α -methyl- Δ^{α} -propenylmalonate*, $CHMe:CMc:CR(CO_2Et)_2$. The structure of the products follows because O_3 gives $MeCHO$ with only traces of CH_2O . The wide b.p. of some of the products is due to *cis-trans* isomerism.

III. If $CH_2R:CR':C(CN)CO_2R''$ is treated with $NaNH_2$ in liquid NH_3 and then with Alk_2SO_4 in PhMe, cleavage and polymerisation occur. Use of Na in Et₂O causes partial reduction. $NaOR'''$ in a $R'''OH$, followed by $AlkBr$ or Alk_2SO_4 gives $CHR:CR':CAlk(CN)CO_2R''$, the structure being proved by production of $RCHO$ by O_3 . The order of preference is $R''' = Pr^{\beta} > Et > Me$, the yield being related inversely to the ease of alcoholysis by the solvent. The following are prepared, those marked * being mixed Et-Pr esters: *Et α -cyano- β -methyl- α -ethyl-*, b.p. 117—117.5°/12 mm., *α -*n*-propyl-**, b.p. 120—122.5°/9 mm., and *α -butyl- Δ^{β} -pentenoate*, b.p. 134—134.5°/9 mm.; *Et α -cyano- $\alpha\beta$ -dimethyl- Δ^{β} -hexenoate**, b.p. 124—126°/16 mm.; *Et α -cyano- β -methyl- α -ethyl-**, b.p. 135—136°/17 mm., *α -*n*-**, b.p. 128—129°/9 mm., and *α -iso-propyl-**, b.p. 133—134°/13 mm., and *α -allyl- Δ^{β} -hexenoate**, b.p. 130—133°/9 mm.; *Et α -cyano- α -methyl- β -ethyl-*, b.p. 112—113°/8 mm., *α -cyano- $\alpha\beta$ -diethyl-**, b.p. 141—143°/22 mm., *α -cyano- β -ethyl- α -*n*-propyl-**, b.p. 132—133.5°/10 mm., and *α -cyano- β -ethyl- α -isopropyl-**, b.p. 129—130°/12 mm., *Δ^{β} -pentenoate*; *Et α -cyano- $\alpha\beta$ -dimethyl-*, b.p. 138—139°/17 mm., and *α -cyano- β -methyl- α -ethyl- Δ^{β} -heptenoate*, b.p. 145—146°/17 mm.; *Me α -cyano- $\alpha\beta$ -dimethyl-**, b.p. 150—152°/22 mm., *α -cyano- β -methyl- α -ethyl-*, b.p. 158—159°/22 mm., *Δ^{β} -octenoate*; *Me α -cyano- $\alpha\beta\delta$ -trimethyl-*, b.p. 130—133°/22 mm., and *α -cyano- $\beta\delta$ -dimethyl- α -ethyl-*, b.p. 137—139°/22 mm., and *α -cyano- α -ethyl- β -propyl- Δ^{β} -hexenoate*. $CH_2R:CR':C(CN)CO_2R''$ are best prepared in $PrOH$, but some interchange of R'' and Pr^{β} occurs.

R. S. C.

Chemically catalysed *cis-trans* isomerisation. C. C. PRICE and R. S. THORPE (J. Amer. Chem. Soc., 1936, 60, 2839—2841).—In light or in the presence of anthracene in the dark, Br isomerises *Et₂ maleate* to *Et₂ fumarate*. Br^+ is probably the catalyst, which functions by a long chain reaction. *cis-trans* Changes are thus not confined to Br atoms.

R. S. C.

Accelerating action of ketones on the Cannizzaro-Tischtschenko reaction. II. Dependence of the accelerating action of ketones on the magnitude of the ketone : CH_2O ratio. M. N. TLITSCHENKO (J. Gen. Chem. Russ., 1938, 8, 766—773; cf. A., 1937, II, 368).—The accelerating effect of ketones on the Cannizzaro reaction of CH_2O in aq. or aq. alcoholic NaOH rises with increasing ketone concn., to a max., corresponding with the no. of CH_2O mols. bound by the given ketone under given conditions (COMe_2 6, cyclohexanone 4, COPhMe 3); this part of the activation-ketone concn. curve is rectilinear. Further increase in ketone concn. inhibits the Cannizzaro reaction, owing to lowering of the effective $[\text{CH}_2\text{O}]$. R. T.

Formation of formaldehyde from percarbonate. A. REŽEK (Ber., 1938, 71, [B], 2486—2487).—Baur's observation (A., 1938, I, 319) of the formation of CH_2O from percarbonate is confirmed by use of dimethylhydroresorcinol in its detection. H. W.

Rate of formation of oximes, phenylhydrazones, and semicarbazones of hydroxy-aldehydes. G. VAVON and P. MONTHEARD (Compt. rend., 1938, 207, 926—927; cf. A., 1938, II, 101).—Interaction of the aldehyde or ketone (1 mol.) with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$, or $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HCl}$ (2 mols.) in 70% EtOH at 0° (aldehydes) or 30° (ketones) is followed by determining the HCl liberated in the first two cases and the unaltered $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ in the last. Many aldehydes and ketones show a marked decrease in the time of half reaction when OH or OMe is α - to CHO or CO . The effect is found at different p_H vals. $\alpha\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ reacts more slowly than COPhMe , which indicates that chelation occurs between the H of CHO and the O of OH , and not vice versa. J. L. D.

Synthesis of glycollic and glyceric aldehydes. A. KUZIN (J. Gen. Chem. Russ., 1938, 8, 592—595).—0.25% glucose and 1% $\text{Ca}(\text{OH})_2$ in 4% CH_2O are incubated at 37° until the reducing power (Fehling's solution at 20°) is max., when the solution is neutralised with H_2SO_4 , made slightly acid with AcOH , and evaporated in vac. to a syrup, from which glyoxal is isolated (4% yield). Glyoxal and aq. CH_2O in presence of $\text{Ca}(\text{OH})_2$ give *dl*-glyceraldehyde in 75% yield. R. T.

Photochemical oxidation of acetone.—See A., 1939, I, 89.

Analyses of mixtures of acetone, *n*-butyl alcohol, and ethyl alcohol.—See B., 1939, 14.

Condensation of ketones with acid chlorides in presence of metallic chlorides. J. COLONGE and K. MOSTAFAVI (Bull. Soc. chim., 1938, [v], 5, 1478—1486; cf. Descudé, A., 1903, i, 735; A., 1930, 713).— $\text{COMeEt}\cdot\text{AcCl}\cdot\text{ZnCl}_2$ (amounts varied) at $15\text{--}20^\circ$ for 24 hr. give a mixture, b.p. $155\text{--}158^\circ$, probably of $\text{CHMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Ac}$ and $\text{CMeEt}\cdot\text{CHAc}$; the two respective semicarbazones have m.p. $182\text{--}183^\circ$ and 131° (cf. Kon *et al.*, A., 1928, 1218). COMePr affords a mixture, b.p. $196\text{--}199^\circ/750\text{ mm.}$, of $\text{CHEt}\cdot\text{CMe}\cdot\text{CHEtAc}$ and $\text{CMePr}\cdot\text{CEtAc}$ (semicarbazone, m.p. $153\text{--}154^\circ$, probably of the former).

Me amyl and hexyl ketone give products, b.p. $150\text{--}153^\circ/30\text{ mm.}$, and $160\text{--}162^\circ/16\text{ mm.}$, respectively. Reactions of $\text{COEt}_2\cdot\text{ZnCl}_2$ and $\text{AcCl}\cdot\text{BzCl}\cdot\text{SOCl}_2$, SO_2Cl_2 , POCl_3 (best), PCl_5 , and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ at $15\text{--}20^\circ$ for 48 hr. are examined. The mixed product, b.p. $186\text{--}190^\circ/757\text{ mm.}$, gives a semicarbazone; m.p. $108\text{--}109^\circ$, probably from $\text{CEt}_2\cdot\text{CMe}\cdot\text{COEt}$ (cf. Kon *et al.*, A., 1931, 1274). The interaction of COEt_2 and POCl_3 at 20° for 48 hr. with various metallic chlorides shows that ZnCl_2 and SnCl_4 are best. COMePr^s , COMeBu^r , or COPr^s does not react with $\text{POCl}_3\cdot\text{ZnCl}_2$. Mechanisms of reactions are discussed. A. T. P.

Hydrogenation of higher ketones with catalysts consisting mainly of nickel or copper. K. KINO (J. Soc. Chem. Ind. Japan, 1938, 41, 259—260b).—The quantities of hydrocarbon and *sec.* alcohol produced in the hydrogenation of ketones at 300° have been determined, using catalysts consisting of Ni or Cu and various other metals. A. LI.

Acid- and alkali-resisting properties of higher ketones, and their solubilities in some organic solvents. K. KINO (J. Soc. Chem. Ind. Japan, 1938, 41, 259b).—When left in contact with the reagent for 142 days, mixed ketones ($\text{C}_{31}\text{--C}_{35}$) are appreciably attacked by conc. H_2SO_4 , slightly by conc. HCl , conc. HNO_3 , and 30% KOH , but not at all by 30% NaOH or dil. acids. The solubility of stearone in org. solvents at three temp. is recorded. A. LI.

Degradation reaction in organic chemistry. A. SCHÖNBERG (Nature, 1938, 142, 997).—Examples of the conversion of $\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}\cdot$ or $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$ into $\cdot\text{CO}\cdot\text{CO}\cdot$ are given. L. S. T.

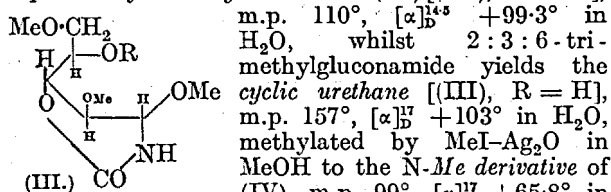
Modern results in the chemistry of carbohydrates. F. MICHEEL (Angew. Chem., 1939, 52, 6—17).—A review in which the following are discussed; configuration, prep. of monosaccharides, reduction products, oxidation products, compounds involving interaction of the CO group, glucosides and ethers, aldehydic and ketonic derivatives, esters, syntheses, position of ring and configuration, oligosaccharides, cellulose, starch, glycogen, Schardinger dextrin, mannans, xylan, agar-agar, pectins, biologically important carbohydrate derivatives, carbohydrate-protein compounds, transition from carbohydrates to the carbocyclic compounds. H. W.

Synthesis of sugars from formaldehyde. VI. Mechanism of the reaction. A. KUZIN (J. Gen. Chem. Russ., 1938, 8, 759—765).—Balezin's dilatometric studies of the reaction of condensation of CH_2O in presence of $\text{Ca}(\text{OH})_2$ (A., 1938, II, 43) are criticised on the grounds that variations in the temp. of the systems were not taken into account. The following reaction mechanism is advanced, as being more in accord with the facts: $\text{OH}\cdot\text{CH}\cdot\text{CR}\cdot\text{OH}$ (I) + $\text{CH}_2(\text{OH})_2$ (II) \rightarrow $\text{OH}\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CR}(\text{OH})_2$ \rightarrow (+MOH) $\text{OH}\cdot\text{CH}_2\cdot\text{CR}(\text{OM})\cdot\text{CR}(\text{OH})_2$ \rightarrow $\text{OH}\cdot\text{CH}\cdot\text{CR}\cdot\text{COR}$ \rightarrow [+ (II)] $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CR}(\text{OH})\cdot\text{COR}$ \rightarrow (I) + $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})_2$ (III); (III) \rightarrow $\text{OH}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ (IV) \rightarrow [+ (II)] $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})_2$. In this reaction $M = 0.5\text{Ca}$, (IV) functions as an autocatalyst, and (I) is a monose having the $\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot$

group, and functioning as a catalyst. Under conditions of biosynthesis (I) may be fructose or ascorbic acid. R. T.

Production of *l*-erythrulose by the action of *Acetobacter suboxydans* on erythritol.—See A., 1938, III, 102.

Descent of the series of methylated sugars by the Weerman reaction. W. N. HAWORTH, S. PEAT, and J. WHETSTONE (J.C.S., 1938, 1975—1980).—3:5:6-Trimethylglucofuranose is oxidised by Br to 3:5:6-trimethyl- γ -gluconolactone, m.p. 44–45°, $[\alpha]_D^{25} + 51.8^\circ \rightarrow +14.1^\circ$ in H₂O in 860 hr., which is converted by liquid NH₃ into 3:5:6-trimethylgluconamide (I), m.p. 144°, $[\alpha]_D^{25} + 34.0^\circ$ in H₂O. Me pentamethylgluconate with NH₃-MeOH yields pentamethylgluconamide (II), m.p. 66°, $[\alpha]_D^{25} + 51.1^\circ$ in H₂O. 2:3:5:6-Tetramethylgluconamide at 0° with aq. NaOCl yields a cyclic urethane (IV) [(III), R = Me],



Mechanism of carbohydrate oxidation. XXIV. Action of aldehydo-*d*-glucose and of aldehydo-*d*-galactose in alkaline solutions. R. J. PLUNKETT and W. L. EVANS (J. Amer. Chem. Soc., 1938, 60, 2847–2852; cf. A., 1937, II, 57).—The amounts of lactic (I) and saccharic (II) acids obtained by 0.5–6N-KOH from aldehydo-*d*-glucose and β -*d*-glucopyranose penta-acetates at 25°, 37.4°, 50°, and 62.5°, and from aldehydo-*d*-galactose and β -*d*-galactopyranose penta-acetates at 25° and 50° are determined. With 3N-KOH they are very similar, but in more conc. KOH the aldehydo-sugars give more (II). The results support the view that pyranoses form aldehydo-sugars before fission to (I). It is postulated that (I) and (II) are obtained by different, but analogous, changes, the rates of which depend on the exact conditions. Susceptibility to alkali usually is a max. at 37.5° and increases only slightly with >3N-KOH. R. S. C.

Mutarotation of *d*-galactose. B. C. HENDRICKS and R. E. RUNDLE (J. Amer. Chem. Soc., 1938, 60, 3007–3009).—The rate of mutarotation of tetramethyl- α -*d*-galactopyranose at 0°, but not at 25°, decreases as equilibrium is approached; $k_1 + k_2$ for “thermal dissociation” from 25° to 0° (Isbell *et al.*, A., 1936, 1209) decreases similarly. Thus, conversion of pyranose into furanose forms is not a general cause of complex mutarotation. R. S. C.

Isolation of an anhydro-*l*-galactose derivative from agar. S. HANDS and S. PEAT (Nature, 1938, 142, 797).—Methylation of agar with Me₂SO₄-NaOH, followed by hydrolysis (MeOH-HCl), fractionation of the glycosides, and methylation (MeI), yields 2:4-dimethyl-3:6-anhydromethyl-1-galactopyranoside, m.p. 82–83°, $[\alpha]_D^{25} + 85.3^\circ$ in CHCl₃, +73° in H₂O, and +77.8° \rightarrow 21° in dil. aq. H₂SO₄, hydrolysed to 2:4-dimethyl-3:6-anhydro-*l*-galactose, m.p. 114°. J. D. R.

Hydrogenating fission of sucrose. R. WEIDENHAGEN and H. WEGNER (Ber., 1938, 71, [B], 2712–2716).—At 170–180°/50 atm., neutral solutions of sucrose (I) in presence of a Ni-Mo catalyst rapidly absorb 4 H₂, after which the rate of absorption diminishes greatly but reaction does not cease. The solution contains acetol (II) due to the intermediate production of AcCHO. The absorption graph indicates that the change is C₁₂H₂₂O₁₁ \rightarrow 4AcCHO \rightarrow 4(II). The neutral character of the solution appears to prevent the further reduction of (II), which is probably present in the desmotropic ethylene oxide form $\text{CH}_2 \text{---} \text{CMe} \cdot \text{OH}$. Attempts to obtain

OH-CH₂-CHMe-OH (III) in a single operation by hydrogenative fission of (I) in presence of Ca(OH)₂ gave mainly (OH-CHMe-CO₂)₂Ca with a little (III) but no (II). Stronger alkali causes an increase in the amount of OH-CHMe-CO₂H whereas weaker alkali [K₂HPO₄, Zn(OH)₂, Mg(OH)₂] is unable to convert (II) into the reducible CO form. Good yields of (III) can be obtained by hydrogenating (I) in a neutral medium until the quantity of H necessary for the formation of (II) has been absorbed. (II) is distilled and the hydrogenation is completed in the distillate made alkaline, preferably with Ca(OH)₂. Addition of alkali to the initial solution at the appropriate stage does not lead to satisfactory results. It appears that at 170°, possibly owing to CO₂ formed as a by-product, (I) is hydrolysed to monosaccharides which at the relatively high temp. rapidly pass into C₃ sugars which lose H₂O to form AcCHO. H. W.

Preparation of rutinose from rutin without aid of enzymes. G. ZEMPLÉN and A. GERECs (Ber., 1938, 71, [B], 2520).—Rutin is hydrolysed by boiling 10% AcOH and rutinose is isolated as the β -hepta-acetate, m.p. 169–170°, $[\alpha]_D^{25} - 27.7^\circ$ in CHCl₃. H. W.

Bioses of hesperidin and of neohesperidin. G. ZEMPLÉN and A. K. TETTAMANTI (Ber., 1938, 71, [B], 2511–2520).—Hesperidin (I) is completely methylated by Me₂SO₄-NaOH followed by Ag₂O-MeI to nonamethylhesperidin, m.p. 180–181°, $[\alpha]_D^{25} - 40.0^\circ$ in CHCl₃, which is hydrolysed by acid to methylated monoses identical in optical activity and reducing power with those derived from completely methylated rutin or methylated rutinose (II). The biose of (I) is therefore identical with (II). Further, fission of (I) with Ba(OH)₂ leads to non-cryst. β -phloroglucinolrutinoside [this gives a non-cryst.

acetate (III), $[\alpha]_D^{20} -44.05^\circ$ in CHCl_3 , also obtained from phloroglucinol and acetobromorutinoside]. The sp. rotation of (III) agrees with that calc. from observation of β -phloroglucinolcellobioside acetate, $[\alpha]_D^{20} -36.0^\circ$ in CHCl_3 , thus showing that (I) is hesperitin- β -rutinoside.

[With, in part, S. FARAGO.] Neohesperidin (IV), m.p. 244° , is hydrolysed to hesperitin, *d*-glucose, and *l*-rhamnose. The restricted action of 0.5% H_2SO_4 leads to a hesperitinglucoside, whereby (IV) is sharply differentiated from (I). The successive action of Me_2SO_4 -NaOH and MeI- Ag_2O on (IV) gives monomethylneohesperidin, $[\alpha]_D^{21} -59.4^\circ$ in EtOH. This is hydrolysed to a mixture of methylated monoses, the reducing power of which is considerably > that of the similar substances obtained from (I) or from rutin. (II) is therefore not present in (IV), which contains a new biose for which the term neohesperidose is proposed. It is probably 1-*l*-rhamnosido-4-*d*-glucose, although the possibility of a 3- or 2-glucose union is not completely excluded. The point of union of the biose to the flavanone is not established. Decamethylrutin, $[\alpha]_D^{20} -32.8^\circ$ in EtOH, is described. H. W.

Arbuscoloside (myricetyl-*d*-galactoside), m.p. 208° .—See A., 1939, III, 219.

Emulsin. XXXV. Glucosides of phenolcarboxylic acids, their enzymic fission and autodecomposition. B. HELFERICH and H. LUTZMANN (Annalen, 1938, 537, 11—21).—Me tetra-acetyl- β -*d*-glucosidosahcylate, m.p. 160.5° (corr.), $[\alpha]_D^{20} -29.3^\circ$ in CHCl_3 , -34° in COMe_2 , is deacetylated by NaOMe in boiling MeOH to Me β -*d*-glucosidosahcylate, m.p. 107° (corr.), $[\alpha]_D^{20} -64.4^\circ$ in H_2O , which is hydrolysed by aq. $\text{Ba}(\text{OH})_2$ at room temp. to β -*d*-glucosidosahcyllic acid (I) ($+0.5\text{H}_2\text{O}$), m.p. 136 — 137° (corr.), $[\alpha]_D^{20} -59.6^\circ$ in H_2O , $[\alpha]_D^{21} -37.0^\circ$ in 7% aq. K_2CO_3 . Treatment of *m*- $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ with acetobromoglucose and of the product with Ac_2O and $\text{C}_2\text{H}_5\text{N}$ yields Me tetra-acetyl- β -*d*-glucosido-*m*-oxybenzoate, m.p. 111 — 112° (corr.), $[\alpha]_D^{20} -28.6^\circ$ in CHCl_3 , whence Me β -*d*-glucosido-*m*-oxybenzoate, m.p. 153 — 154° (corr.), $[\alpha]_D^{20} -74.1^\circ$, and the free acid. β -*d*-Glucosido-*p*-oxybenzoic acid has m.p. 211 — 212° (corr.), $[\alpha]_D^{21} -81.4^\circ$ in H_2O . β -*d*-Glucosido-*o*-coumaric acid ($+1\text{H}_2\text{O}$), m.p. 245° (corr.; decomp.), $[\alpha]_D^{21} -76.5^\circ$ in 50 vol.-% EtOH [tetra-acetate, m.p. 187 — 188° (corr.), $[\alpha]_D^{21} -56.3^\circ$ in CHCl_3], is converted by CH_3N_2 into its Me ester, m.p. 189 — 190° (corr.), $[\alpha]_D^{20} -72.2^\circ$ in 50 vol.-% EtOH [tetra-acetate, m.p. 125 — 126° (corr.), $[\alpha]_D^{21} -53.5^\circ$ in CHCl_3]. Coumarin is converted by 2*N*-NaOH and acetobromoglucose into tetra-acetyl- β -*d*-glucosidocoumarinic acid, m.p. 155 — 156° (corr.), $[\alpha]_D^{18} +14.5^\circ$ in CHCl_3 . The corresponding Me ester, m.p. 110° (corr.), $[\alpha]_D^{21} +7.3^\circ$ in CHCl_3 , is hydrolysed to Me β -*d*-glucosidocoumarinate, m.p. 98 — 99° (corr.), $[\alpha]_D^{22} -63.6^\circ$ in H_2O , which yields a non-cryst. acid (II). Among the free acids the derivative of *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is most rapidly hydrolysed by enzymes whilst there is practically no difference in the case of fission of the esters of the simple phenolcarboxylic acids. There appears to be no parallelism between the possibility of lactone formation and the rate of hydrolysis. Provided that

a neutral or alkaline solution is assured by buffering there is no evidence of autodecomp. at 60° . Solutions of the free acids (p_H 2.4—2.9) are also stable with the exception of that of (I) which is affected even at room temp. On the other hand the possibility of lactone formation does not induce the autodecomp of (II).

H. W.

Determination of uronic anhydride residues in polysaccharides. W. G. CAMPBELL, E. L. HIRST, and G. T. YOUNG (Nature, 1938, 142, 912—913; cf. A., 1938, III, 545).—Glucose, fructose, sucrose, maltose, mannose, and xylose, potato, rice, and wheat starches, etc., but not mannitol, give small amounts of CO_2 (0.2—1%) when heated with aq. HCl. For starches, no structural significance can be attached to these small yields of CO_2 , whilst for other polysaccharides yields >1% may be untrustworthy as an indication of the presence of uronic anhydride. The claim advanced previously (A., 1935, 797) that certain wood starch preps. contain uronic anhydride is not invalidated; only the numerical results are affected. L. S. T.

Significance of "end-group" determination in polysaccharides. E. HUSEMANN (Papier-Fabr., 1938, 36, 51, 559—563).—A discussion of relevant literature. A. T. P.

Action of chlorine water on β -amyloses. H. H. FLETCHER and T. C. TAYLOR (J. Amer. Chem. Soc., 1938, 60, 3018—3025).— β -Amylose is treated with Cl_2 at $p_H < 10$ and the reaction stopped by C_2H_4 at different times; the reducing power and "alkali-labile val." (Taylor *et al.*, A., 1935, 1064) decrease gradually, but η remains const.; this is due to oxidation of terminal CHO to CO_2H . In neutral or acid solution, there is at first only slight change, then a sudden, large rise in reducing power and alkali-labile val. and a large decrease in η ; thereafter, alkali-labile val. slowly decreases, but the reducing power and η remain const. In these cases the first action is penetration of H_2O into the micelle, catalysed by HOCl; then the micelles suddenly disrupt (lower η) and thus expose CHO which was previously masked. During reaction the p_H decreases and even partial prevention of this change by buffering increases the final decreases in alkali-labile val. and reducing power. Tapioca, potato, and maize starches behave similarly, but not identically. Longer grinding increases the rates of change. The reducing power and alkali-labile val., but not η , of glucose are decreased by Cl_2 , but the reaction is not quite analogous to that of starch. R. S. C.

Polysaccharide produced from sucrose by *Betabacterium vermiforme*.—See A., 1939, III, 102.

Dextran produced from sucrose by *Betacoccus arabinosaceus haemolyticus*.—See A., 1939, III, 102.

Methylated starch. K. FREUDENBERG and H. BORPPEL (Ber., 1938, 71, [B], 2505—2511).—Starch is readily methylated with Na, NH_3 , and MeI if the mixture is kept heterogeneous. It is necessary to remove NaI periodically and to reach at least a 20% OMe content during the first operation; otherwise gel formation

or, possibly, dissolution results. The product is purified by hot H_2O , whereby the final val. (45.6% OMe) is readily attained. Alternatively, after a certain OMe content has been reached the formation of slime can be avoided by operating in solution in $NHMe_2$, $NHEt_2$, or, preferably, NH_3 . Amylose and amylopectin are methylated similarly and the products cannot be distinguished from one another. Terminal group determinations of the Me_3 ethers of the three compounds yield 3.2–3.4% of tetramethylglucose (I), 1.8–2.2% of dimethylglucose (II), 91% of trimethylglucose (III) (calc. as anhydride), and 4% of distillation residue. 5% of terminal groups appear to be present and (II) and (III) are present in the ratio 1:1. (I) is identified as such. Trimethylglucoses other than (III) do not appear to be present.

H. W.

Cellulose hydrolysis by ethyl mercaptan. III. M. L. WOLFRAM and J. C. SOWDEN (J. Amer. Chem. Soc., 1938, 60, 3009–3013; cf. A., 1938, II, 265).—Cotton linters is hydrolysed by 41% HCl with and without $EtSH$, and the degree of polymerisation is calc. by η and the S content of the product at various times. η gives consistently the higher mol. wts.

R. S. C.

Methylation of cellulose. K. FREUDENBERG, E. PLANKENHORN, and H. BOPPEL (Ber., 1938, 71, [B], 2435–2438; cf. A., 1937, II, 370).—Cellulose (I) can be completely methylated by repeated treatment with Na and MeI in liquid NH_3 . The methylation of (I), which contains 40% OMe introduced by the action of cold Me_2SO_4 and KOH, can be rapidly completed by this method. Such an incompletely methylated (I) gives a very viscous solution in $CHCl_3$ but after treatment with Na–MeI–liquid NH_3 the viscosity (η) diminishes markedly. Methylcellulose, prepared exclusively in NH_3 , has invariably a low η . Treatment of highly viscous (I) at -70° under NH_3 with Na or $NaNH_2$ is sufficient to diminish η . Treatment of 2:3:6-trimethylglucose (II) with cold $MeOH$ –3% HCl and of the product with Ag_2CO_3 gives, after distillation, a glucoside mixture with nearly the expected $[\alpha]_D$ in H_2SO_4 . If the mixture is warmed before removing the HCl the val. of $[\alpha]_D$ increases with the temp. employed and with the duration of heating. Products derived from methyl-cellulose or -starch show precisely similar behaviour. If the glucoside mixtures of highest $[\alpha]_D$ are hydrolysed with dil. HCl the product is essentially (II). Glucosides with varying final $[\alpha]_D$ do not differ from one another essentially in b.p. The phenomena are not explained but it is advocated that treatment of polysaccharides with $MeOH$ –HCl should be used with caution and that prolonged heating during glucosidation should be avoided as far as possible.

H. W.

Constitution of organic salts of hexamethylenetetramine. P. BOUCHEREAU (J. Pharm. Chim., 1938, [viii], 28, 484–489).—When alcoholic solutions of $(CH_2)_6N_4$ and org. acids are mixed at or below 80° the corresponding salts are obtained, whilst if aq. solutions and higher temp. are used then double NH_4 $(CH_2)_6N_4$ salts are formed. The following salts of $(CH_2)_6N_4$ are described: *salicylate* and double NH_4 *salicylate*, *citrate* and double NH_4 *citrate*, *benzoate*,

m.p. 132° , and double NH_4 *benzoate*, *m.p.* 125° , *diethylbarbiturate*, *m.p.* 163 – 164° , and double NH_4 *methylenecitrate*, *m.p.* 163° . J. N. A.

Chemical, physiological, and neutralising action of hexamethylenetetramine on dichlorodiethyl sulphide (Ypérite or Lost). P. BRUÈRE and P. BOUCHEREAU (J. Pharm. Chim., 1938, [viii], 28, 490–492).—Aq. $(CH_2)_6N_4$ rapidly diffuses into tissues, and can be used to counteract the effects of mustard gas, with which it reacts in presence of H_2O forming NH_4Cl , the corresponding glycol, and trace of CH_2O .

J. N. A.

Crystalline triethanolamine iodo-mercuroate. H. GRIFFON (Bull. Soc. chim., 1938, [v], 5, 1694–1699).— $N(CH_2CH_2OH)_3$ gives no ppt. with Mayer's reagent, but with Valser's more conc. reagent in neutral or slightly acid solution ($>0.03N$.) gives the salt, B, HI, HgI_2 (photomicrograph). R. S. C.

Aminopentane-polyols. J. BARBIÈRE and J. MATTI (Bull. Soc. chim., 1938, [v], 5, 1565–1567).— $C(CH_2OH)_4$ and HBr (d 1.78) at 120° for 15 hr. afford $C(CH_2Br)_2(CH_2OH)_2$ and β -bromomethyl- β -hydroxymethylpropane- α -diol, *m.p.* 76° , converted by $NPhMe_2-C_6H_6$ at 150° for 15 hr. into β -dimethylaminoethyl- β -hydroxymethylpropane- α -diol, *m.p.* 51 – 52° , b.p. 178 – $182^\circ/4$ mm. (*hydrochloride*, *m.p.* 125.5°). Similarly, $CMe(CH_2OH)_3$ and HBr at 100° for 15 hr. give β -methyl- β -bromomethylpropane- α -diol, *m.p.* 71° , b.p. 151 – $152^\circ/15$ mm., converted (140°) into the corresponding β - NMe_2 -compound, b.p. $128^\circ/15$ mm. (*hygroscopic hydrochloride*) (corresponding β - NEt_2 -compound, b.p. $174^\circ/2.3$ mm.). A. T. P.

Affinity of amino-acids and polypeptides for acids, bases, and zwitterions.—See A., 1939, I, 80.

Reversible action of oxidised phenols in the deamination of certain amino-acids. S. S. HUBARD (J. Biol. Chem., 1938, 126, 489–492).—The amount of deamination of glycine by tyrosinase and *p*-cresol (I) in aerated buffer solutions at p_H 7.8 shows that (I) functions reversibly to a limited extent. It probably combines with the end-products, since the NH_3 recovered is $<$ that corresponding with the amount of deamination. Data of Robinson *et al.* (A., 1925, i, 745) are consistent with this theory.

A. LI.

Optically active amino-acids. VII. S. BERLINGOZZI and (SIGNA.) R. LENOCI (Gazzetta, 1938, 68, 721–728).—*l*- α -Bromoisovaleryl-*l*-asparagine (I) (A., 1926, 819) with boiling 25% HCl gives *l*- α -bromoisovaleric acid (II) and aspartic acid. Similarly the *d*-isomeride of (I) gives the *d*-isomeride of (II). With boiling 4N-HCl, however, (I) gives mainly *l*- α -bromoisovalerylaspartic acid (III), *m.p.* 167° , $[\alpha]_D^{20} -10.2^\circ$ (Na_2 salt in H_2O), with some (II). *d*- α -Bromoisovalerylaspartic acid, *m.p.* 158 – 159° , $[\alpha]_D^{20} +12.1^\circ$ (Na_2 salt in H_2O), is obtained similarly. *l*-Aspartic acid and *r*- α -bromoisovaleryl-*l*-asparagine yield a product from which impure (III) is fractionated.

E. W. W.

S-Cysteinossuccinic acid. E. J. MORGAN and E. FRIEDMANN (Biochem. J., 1938, 32, 2296–2298; cf. A., 1938, III, 614).—The amorphous reaction

product from *l*-cysteine and maleic acid (cf. A., 1938, II, 216) separates from MeOH to give *S*-cysteino-succinic acid, m.p. 134–135° (decomp.) after softening at 102°, $[\alpha]_D -29.8^\circ$ in H₂O, racemised by boiling AcOH. *S*-Glutathionosuccinic acid (*loc. cit.*) with boiling 25% H₂SO₄ gives partly racemised *S*-cysteino-succinic acid. The inhibition by maleic acid of enzyme reactions induced by SH-compounds may be due to the above type of reaction. J. L. D.

Synthesis of natural creatinephosphoric acid. K. ZEILE and G. FAWAZ (Z. physiol. Chem., 1938, 256, 193–196; cf. A., 1939, II, 11).—Creatine at 0° in aq. NaOH with POCl₃ gives a 28% yield of creatinephosphoric acid (separated as Ca salt, C₄H₈O₅N₃PCa, 4H₂O) identical with the natural acid. W. McC.

New derivatives of the silyl radical. H. J. EMELEUS and N. MILLER (Nature, 1938, 142, 996–997).—SiH₃Cl reacts spontaneously with NH₂Me or NH₂Et to give *methyl*-, NMe(SiH₃)₂, b.p. 32.3°, or *ethyl-disilylamine*, b.p. 65.9°, which are stable in air, but are quantitatively hydrolysed by alkali, and decomposed by HCl. Cold NMe₃ and SiH₃Cl yield a stable *solid*, NMe₃SiH₃Cl (I), decomposed by H₂O to disiloxane and NMe₃HCl. In moist air the final products are silicic acid and NMe₃HCl, but the intermediate products give solutions with strong reducing properties. (I) is hydrolysed NMe₃SiH₃Cl + 3NaOH = Na₂SiO₃ + NaCl + NMe₃ + 3H₂. (I) is a convenient silylating agent; e.g., with alcohols it forms volatile silyl alkyl ethers, which can easily be isolated. At room temp. SiH₃Cl and NHMe₂ give the *compound*, NSiH₃Me₂, which appears to form an unstable quaternary salt with excess of SiH₃Cl. L. S. T.

Alkyl and aryl esters of orthosilicic acid. III. **Synthesis of triethoxyallylmonosilane.** K. ANDRIANOV and M. KAMENSKAJA (J. Gen. Chem. Russ., 1938, 8, 969–971).—CH₂:CH·CH₂Br, Mg, and Si(OEt)₄ yield *triethoxyallylmonosilane*, b.p. 172–178°. R. T.

Course of reaction giving rise to acetylene-bismagnesium bromide.—See A., 1939, I, 85.

Complexes of magnesium chloride with organic oxygen compounds. A. S. OSOKIN (J. Gen. Chem. Russ., 1938, 8, 583–587).—The following *compounds* are obtained by heating anhyd. MgCl₂ with anhyd. org. compounds containing O in C₆H₆ or light petroleum: MgCl₂·6C₅H₁₁·OH, MgCl₂·2COMe₂, MgCl₂·furfuraldehyde, MgCl₂·10Bu^oCO₂H, MgCl₂·2C₅H₁₁·OAc, MgCl₂·12Ac₂O. R. T.

Action of magnesium *tert*-butyl chloride with acetyl chloride. F. C. WHITMORE and W. R. WHEELER (J. Amer. Chem. Soc., 1938, 60, 2899–2900).—Addition of MgBu^oCl to an excess of AcCl in Et₂O gives COMeBu^o (I) 17, CHMeBu^o·OAc 8, EtOAc 9, *iso*-C₄H₈ 6.6, mesityl oxide (II) (origin unknown) 6.6, and *iso*-C₄H₁₀ [probably derived by reaction of (I) and (II) with MgBu^oCl] 23.6%. The EtOAc is proved to be formed from the AcCl and Et₂O under the influence of the anhyd. MgCl₂ formed. R. S. C.

Activity of cadmium ion in organic salts of cadmium.—See A., 1939, I, 80.

Mechanism of oxidation of organic substances with selenium dioxide. III. **Oxidation of metallo-organic compounds.** N. N. MELNIKOV and M. S. ROKITZKAJA (J. Gen. Chem. Russ., 1938, 8, 834–838).—SeO₂ and HgR₂ yield (HgR)₂SeO₃ (R = Et; R = *Pr*, decomp. 220–230°; R = *Bu*, decomp. 172°; R = *iso*-C₆H₁₁, decomp. 240–250°). MPh₃ (M = P, As, Sb) reacts: 3MPh₃ + SeO₂ → 2MPhO + MPh₂Se. R. T.

Tetramethylplatinum and hexamethyldiplatinum. H. GILMAN and M. LICHTENWALTER (J. Amer. Chem. Soc., 1938, 60, 3085–3086).—*Tetramethylplatinum*, *cryst.*, obtained in 46% yield from PtMe₃I and NaMe or as a by-product from PtCl₄ and MgMeI, is converted into PtMe₃Cl by HCl. *Hexamethyldiplatinum*, *cryst.*, obtained in 60% yield from PtMe₃I and K in C₆H₆, is converted by I in Et₂O into PtMe₃I. R. S. C.

Isomerism of platinum ethylene chlorides.—See A., 1939, I, 94.

Compounds of rhodium and iridium with dimethylglyoxime.—See A., 1939, I, 93.

Catalytic transformations of 2-methyl-1 : 2 : 2-dicyclo-Δ⁵-heptene and of 2-methyl-1 : 2 : 2-dicycloheptane. B. A. KAZANSKI and N. G. TSCHERNOVA (J. Gen. Chem. Russ., 1938, 8, 651–653).—2-Methyl-[1 : 2 : 2]-dicyclo-Δ⁵-heptene is converted into unidentified substances of high mol. wt. when passed over C-Pt at 300°; the catalyst is thereby inactivated. 2-Methyl-[1 : 2 : 2]-dicycloheptane and H₂ yield when passed over C-Pt at 310° a mixture of paraffins and cyclopentanes, together with small amounts of PhMe and *m*-xylene. R. T.

Hydrogenation of aromatic hydrocarbons by the action of calcium-ammonia. II. B. A. KAZANSKI and N. F. GLUSCHNEV (J. Gen. Chem. Russ., 1938, 8, 642–650; cf. A., 1937, II, 489).—Ca(NH₃)₆ reduces PhMe, PhEt, *o*-, *m*-, and *p*-xylene, *s*-C₆H₅Me₃, tetrahydronaphthalene, or Δ^{1:4}-cyclohexadiene at room temp. to 1-methyl-, 1-ethyl-, 1 : 2-(+1 : 6-), 1 : 3-, and 1 : 4-dimethyl-, and 1 : 3 : 5-trimethyl-Δ¹-cyclohexene, Δ^{1:9}- and Δ^{9:10}-octahydronaphthalene, or cyclohexene, respectively. R. T.

Possibility of existence of cyclic systems having a triple linking. II. **Synthesis of cyclooctinene.** N. A. DOMNIN (J. Gen. Chem. Russ., 1938, 8, 851–868).—*cyclo*Octanone and PCl₅ in light petroleum at >40° yield 1-*chloro*-Δ¹-cyclooctene, b.p. 64–68°/10 mm., the dibromide of which when heated with 20% KOH in EtOH gives 1-*chloro*-2-*bromo*-Δ¹-cyclooctene, b.p. 96–100°/3 mm. This with Na in Et₂O (6 days at room temp.) affords cyclooctinene (I), b.p. 72–76°/100 mm.; small amounts of a *dimeride*, b.p. 100–105°/3 mm., of (I), and of tri(hexamethylene)-benzene are also formed. R. T.

Compound of aluminium bromide with benzene.—See A., 1939, I, 81.

Kinetics of cracking of aromatic hydrocarbons under pressure.—See A., 1939, I, 85.

Photochemical addition of bromine to bromobenzene.—See A., 1939, I, 89.

New aromatic fluoro-derivatives. (MME.) A. C. DE DEGIORGI and E. V. ZAPPI (Bull. Soc. chim., 1938, [v], 5, 1441—1446).—An account of work previously reviewed (A., 1938, II, 482). A. T. P.

Dehydrogenation of 1-vinyl- Δ^3 -cyclohexene. J. M. SLOBODIN and P. N. KRASNOBAEVA (J. Gen. Chem. Russ., 1938, 8, 738—739).—1-Vinyl- Δ^3 -cyclohexene passed over a Ni- Al_2O_3 catalyst at 300—320° yields chiefly PhEt with traces of styrene. R. T.

Hydrogen fluoride as condensing agent. II. Alkylation of benzene by olefines. III. Alkylation of aromatic [compounds] with aliphatic halides. J. H. SIMON and S. ARCHER. **IV. Reaction of cyclopropane with benzene.** J. H. SIMONS, S. ARCHER, and (MISS) E. ADAMS. **V. Reactions of compounds containing oxygen and reactions of tertiary halides with olefines.** J. H. SIMONS, S. ARCHER, and H. J. PASSINO (J. Amer. Chem. Soc., 1938, 60, 2952—2953, 2953—2954, 2955—2956, 2956—2957; cf. A., 1938, II, 225).—II. C_6H_6 with "relatively dry" HF and C_3H_6 , $\text{CH}_2\text{:CMe}_2$, CHMe:CHEt , CHMe:CMe_2 , or cyclohexene gives PhPr^s (84), PhBu^r (44) + $\text{C}_6\text{H}_4\text{Bu}^r_2$ (41), m.p. 77—78°, (β - + γ -) $\text{C}_6\text{H}_{11}\text{Ph}$ (47), CPhMe_2Et (21) + $\text{C}_6\text{H}_4(\text{CMe}_2\text{Et})_2$ (60), and cyclohexylbenzene (62%), respectively. Polymerisation and addition of HF may also occur, but were not detected.

III. With Bu^rCl or CMe_2EtCl and HF at 0°/1 atm. C_6H_6 gives PhBu^r (10) + $\text{C}_6\text{H}_4\text{Bu}^r_2$ (60) and CPhMe_2Et (41.5) + $\text{C}_6\text{H}_4(\text{CMe}_2\text{Et})_2$ (21.5%), respectively. C_{10}H_8 in CCl_4 gives similarly $\text{C}_{10}\text{H}_7\text{Bu}^r$, b.p. 142—143°/14 mm. (46%), and two $\text{C}_{10}\text{H}_8\text{Bu}^r_2$, m.p. 148° (8%) and m.p. 80—81° (28%). PhMe , Bu^rCl , and HF give 75% of p - $\text{C}_6\text{H}_4\text{MeBu}^r$. Pr^sCl , C_6H_6 , and HF react at 25°, giving a small yield of polyisopropylbenzenes, b.p. 155—175°/740 mm. Pr^sBr , HF, and C_6H_6 react only at 80°, giving 48% of a mixture of PhPr^s (12%) and PhPr^s (88%).

IV. C_6H_6 , cyclopropane, and HF give PhPr^s (42), $\text{C}_6\text{H}_4\text{Pr}^s_2$ (20), and $\text{C}_6\text{H}_3\text{Pr}^s_3$ (3%). Pr^s derivatives are not formed, which indicates that the reaction mechanism is ionic. PhPr^s and PhPr^s are distinguished by their sulphonamides, m.p. 102.5° and 98°, respectively (eutectic, 57 : 43, m.p. 73°).

V. Bu^rCl , CHMe:CMe_2 , and HF give a mixture, including 18% of an olefinic product, b.p. 63—65°/19 mm. Bu^rCl , cyclohexene, and HF give 31% of an unsaturated product, b.p. 40—42°/18 mm., 141.5—142°/739 mm., and <10% of triisobutene. With much HF, C_6H_6 and Bu^rOH give 3% of PhBu^r and 8% of $\text{C}_6\text{H}_4\text{Bu}^r_2$, m.p. 78—78.5°. Bu^rCl and PhOH give 85% of p - $\text{C}_6\text{H}_4\text{Bu}^r\text{OH}$, and Bu^rCl and Et furoate give 54% of Et 5-*tert*-butyl-2-furoate, b.p. 116—117°/16 mm. HF owes its catalytic ability to (a) its proton-donating properties, (b) its ability to add to org. compounds to give complexes, and (c) loss of F from C-F owing to the high energy of formation of HF.

R. S. C.

Condensation of aliphatic alcohols with aromatic compounds in the presence of aluminium chloride. II. Tertiary aliphatic alcohols and benzene. R. C. HUSTON, W. B. FOX, and M. N. BINDER (J. Org. Chem., 1938, 3, 251—260; cf. A., 1936, 602).—Aliphatic *tert*. alcohols condense readily

with C_6H_6 in presence of AlCl_3 to give *tert*-alkylbenzenes, but, if branching of the chain occurs at the C next to the C-OH, the yield is lowered owing to the tendency to form olefines and chlorides. The reaction was studied with Bu^rOH , $\text{CMe}_2\text{Et}\cdot\text{OH}$, three *tert*- $\text{C}_6\text{H}_{13}\cdot\text{OH}$, and seven *tert*- $\text{C}_7\text{H}_{15}\cdot\text{OH}$. B.p., [M], *d*, and parachors are reported for all the products; relationships are discussed; in general they follow accepted rules. The following are new. β -Phenyl- $\beta\gamma$ -dimethyl-, b.p. 86—87°/15 mm., and $\beta\gamma\gamma$ -trimethyl-*n*-butane, b.p. 105—108°/20 mm.; β -phenyl- $\beta\gamma$ -dimethyl-*n*-pentane, b.p. 105—107°/20 mm.; β -phenyl- β -methyl-*n*-hexane, b.p. 106—109°/20 mm. β -Phenyl- β -ethyl- and γ -phenyl- γ -ethyl-*n*-pentane have b.p. 106—107°/20 mm. and 107—108°/20 mm. (225—226°/745 mm.), respectively (cf. lit.). R. S. C.

Products of condensation of benzene with cyclopentene in presence of aluminium chloride. S. S. NAMETKIN and E. S. POKROVSKAJA (J. Gen. Chem. Russ., 1938, 8, 699—713).—cyclopentene (I) and C_6H_6 in presence of AlCl_3 yield cyclopentyl- (II), *p*- (III), m.p. 42—43°, and *m*-di-cyclopentyl- (IV), b.p. 154—156°/4 mm., and 1 : 3 : 5-tri-cyclopentylbenzene (V), m.p. 60—61°. (III) and (IV) are also prepared from (I) and (II), and (V) from (I) and (IV), a liquid isomeride of (V), b.p. 191—193°/4 mm., also being formed. (II) and excess of (I) yield tetracyclopentylbenzene, m.p. 200—201°. Hydrogenation of the products (active C catalyst, at 180°) yields: from (II) cyclopentylcyclohexane, and from (III), (IV), and (V) respectively 1 : 4-, m.p. 86—86.5°, and 1 : 3-di-, b.p. 146—148°/4 mm. m.p. 28—29°, and 1 : 3 : 5-tri-cyclopentylcyclohexane, b.p. 194—195°/4 mm., m.p. 20—21°. The solubilities of the above products in H_2SO_4 of different concns., lævulic acid, light petroleum, and $\text{C}_2\text{H}_4\text{Cl}_2$ are determined. R. T.

Action of aromatic diazo-compounds on unsaturated compounds. IV. Aromatic and aromatic-aliphatic hydrocarbons. A. P. TEREENTIEV and L. L. GOMBERG (J. Gen. Chem. Russ., 1938, 8, 662—668).—Styrene and dimethylstyrene do not react with diazotised *p*- or 2 : 4-di-nitroaniline; the latter gives a compound, m.p. 110—112° (decomp.), with indene. R. T.

Structure and absorption spectra of polymerides of aromatic compounds having a propenyl or isopropenyl side-chain.—See A., 1939, I, 7.

Isomeric change in stilbenes.—See A., 1939, I, 86.

Application of the electronic theory to organic chemistry. IX. Mechanism of the reaction of formation of naphthalene from 1-nitronaphthalene. A. M. BERKENHEIM and M. P. FILIMONOV (J. Gen. Chem. Russ., 1938, 8, 608—624).—The reaction between 1- $\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ (I) and $(\text{NH}_4)_2\text{SO}_3$ (II) is shown, on theoretical grounds, to proceed thus: (I) + (II) \rightarrow 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{NH}_4$ (III) + NH_4NO_2 ; (III) + $\text{H}_2\text{O} \rightarrow \text{C}_{10}\text{H}_8 + \text{NH}_4\text{HSO}_4$; (I) + (II) $\rightarrow \alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{SO}_3\text{NH}_4$ (IV) \rightarrow 1 : 4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{NH}_4$ (V) \rightarrow (+ H_2O) $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (VI) + NH_4HSO_4 . This mechanism is confirmed by the following observations: the yield of (IV) falls from 60% to nil from the 2nd to the 22nd hr. of heating the reaction mixture; over

the same period that of (V) rises from 7 to a max. of 50%, thereafter falling at the same rate as that of (VI) rises. Max. production of $C_{10}H_8$ takes place between the 12th and 15th hr. of reaction, while (I) and (II) are still present in significant amounts. $C_{10}H_8$ is not obtained from $1-C_{10}H_7NO$ or $\alpha-C_{10}H_7NH\cdot OH$ and (II) under the conditions of the above reaction. Each of the above constituent reactions was realised experimentally, with the exception of the rearrangement of (IV) to (V). R. T.

Spectrographic studies by means of corrected Hartley figures. meso-Derivatives of anthracene. C. DUFRASSE and J. HOUPIILLART (Bull. Soc. chim., 1938, [v], 5, 1633—1637; cf. A., 1938, I, 373).—Data are recorded for the 9:10- Br_2 -, $-(NO_2)_2$ -, and $-(OMe)_2$ -, and 10-iodo-9-phenyl derivatives, and for 9-phenylanthracene-10-carboxylic acid and its Me ester. C. R. H.

Spectrographic investigation of the "active" forms of 9:10-diphenylanthracene. C. DUFRASSE and J. HOUPIILLART (Bull. Soc. chim., 1938, [v], 5, 1628—1633).—The yellow colour obtained by heating solutions of the compound is not due to radical formation (cf. Ingold and Marshall, A., 1927, 141), but to an increase in absorptive power with rise in temp. If new mols. are formed they are insufficient to affect the visible spectrum. C. R. H.

Phenanthrene series. XX. Nitration of 9:10-dihydrophenanthrene. J. W. KRUEGER and E. MOSSETTIG (J. Org. Chem., 1938, 3, 340—346).—9:10-Dihydrophenanthrene and HNO_3 (d 1.5) in AcOH at 29—33° give 65% of the 2-, m.p. 81—82°, and 3—4% of the 4- NO_2 -derivative, m.p. 97—98° (resistant to CrO_3). H_2-PtO_2 in EtOH then yields the 2-, m.p. 49—52° (converted into the known 2-OH-compound), and 4- NH_2 -derivative (I), m.p. 53—54° (corr.) [hydrochloride, m.p. 270—273° (decomp.; vac.; corr.)]. With $NO\cdot SO_3H$ (I) yields the diazonium sulphate, converted by hot H_2O into 4-hydroxy-9:10-dihydrophenanthrene, m.p. 72—74° (corr.), the oily Me ether of which with Pd-black at 300° in N_2 gives only a little phenanthrene. The Ac_2 derivative, m.p. 100—103°, of (I) with Pd-black in N_2 gives 4-acetamidophenanthrene, m.p. 196—197°, hydrolysed to 4-amino-phenanthrene, m.p. 62.5—63.5° (lit.; 104—105°) [Bz derivative, m.p. 216—218° (corr.)], which yields the known 4-OH- and 4-OMe-derivatives. Attempts to prepare a naphthoquinoline from (I) by the Skraup reaction failed. R. S. C.

Mechanism of aromatic bromination. C. C. PRICE and C. E. ARNTZEN (J. Amer. Chem. Soc., 1938, 60, 2835—2837).—Determination of Br and acid shows that bromination of phenanthrene (I), when catalysed by I in the dark, follows the equation, $d[C_{14}H_9Br]/dt = k[C_{14}H_{10}][Br]^{1/2}[I]^{2/3}$, k being $6.7-5.4 \times 10^{-6}$. Bromination of (I) thus exactly resembles that of C_6H_6 (cf. A., 1937, II, 12). Both involve addition of Br^+ , followed by elimination of H^+ under the influence of the catalyst (cf. loc. cit.). The reaction rate decreases with larger amounts of I, probably due to removal of Br by the reaction, $Br_2 + 2I \rightleftharpoons 2BrI$; this assumption leads to $K_{Ibr} = 15-30$, in good agreement with the val. (19.9) calc.

by extrapolation from Bodenstein and Schmidt's expression (A., 1926, 1100). R. S. C.

Reaction of bromine with various samples of phenanthrene. C. C. PRICE, C. E. ARNTZEN, and C. WEAVER (J. Amer. Chem. Soc., 1938, 60, 2837—2839).—Pure phenanthrene (A), m.p. 99—99.5°, is readily obtained from crude material by conversion into the dibromide and treatment thereof with Zn dust in EtOH at 50—60°. With Se at 300—320° this gives a material (B), m.p. 99.5—100°. With Br (at. reaction) (B) reacts only very slowly [cf. the synthetic material of Fieser *et al.* (A., 1936, 203), also prepared by Se]. In presence of anthracene in the dark 1 mol. of Br reacts with (A) or (B) for each mol. reacting with the anthracene. (B) inhibits the at. chain reaction of Br with other samples. Thus, Se treatment introduces an inhibitor, which breaks the chain. R. S. C.

Synthesis of phenanthrene derivatives. I. 9-Phenyl- and 9-p-tolyl-phenanthrene. C. K. BRADSHAW and A. K. SCHNEIDER (J. Amer. Chem. Soc., 1938, 60, 2960—2962).—9-Substituted phenanthrenes are prepared by elimination of $H_2O + ROH$ from $o-C_6H_4Ph\cdot CAr(OH)\cdot CH_2\cdot OR$. $o-C_6H_4Ph\cdot MgI$ (I) and $OMe\cdot CH_2\cdot CN$ in $Et_2O-C_6H_6$ give 2- ω -methoxyacetyldiphenyl, b.p. 159—162°/4 mm., converted by $MgArBr$ into 2- α -hydroxy- β -methoxy- α -phenyl- and - α -p-tolyl-ethylidiphenyl, oils, which in conc. H_2SO_4 at room temp. give 9-phenyl- (II), m.p. 104—105° (picrate, m.p. 114°), and 9-p-tolyl-phenanthrene, m.p. 90—91° (picrate, m.p. 126—127°). $COPh\cdot CH_2\cdot OPh$ and (I) in $Et_2O-C_6H_6$ give 2- α -hydroxy- β -phenoxy- α -phenylethylidiphenyl, m.p. 94—95°, converted into (II) by $HBr\cdot AcOH$, but by conc. H_2SO_4 at 100° into a substance, $C_{26}H_{20}O$, m.p. 150—152°. R. S. C.

Preparation of $\Delta^{3:5}$ -cholestadiene. K. HATORI (J. Amer. Chem. Soc., 1938, 60, 3082).— ψ -Cholestene dibromide and $AgNO_3$ in C_5H_5N give $\Delta^{3:5}$ -cholestadiene, m.p. 79—80°, $[\alpha]_D^{25} -68.7^\circ$ (cf. Stavely *et al.*, A., 1937, II, 289). R. S. C.

Synthesis of 2:6:8:12-tetraphenyl-5:11-di-p-diphenylnaphthacene and its photo-oxide. D. DUVEEN and A. WILLEMART (Compt. rend., 1938, 207, 1226—1227; cf. A., 1936, 1499).— $p-LiC_6H_4Ph$ with $CPh\cdot C\cdot CO_2Me$ affords γ -phenyl- α -di-p-diphenylpropargyl alcohol, m.p. 143°, converted by PCl_5 into an unstable chloride which, when heated, loses HCl and dimerises to form 2:6:8:12-tetraphenyl-5:11-di-p-diphenylnaphthacene (I), m.p. 320° and 380° after solidification. This is thermochromic in the solid state, shows absorption max. (in C_6H_6) at 5450, 5100, and 4800 Å., and when insulated in solution forms a photo-5:12-oxide, $C_{66}H_{44}O_2$, which when heated loses O_2 (70%) and regenerates (I). J. L. D.

Synthesis of chrysene derivatives. M. S. NEWMAN (J. Amer. Chem. Soc., 1938, 60, 2947—2951).—General methods of preparing 2-substituted chrysene derivatives are described. Prep. of $CH_2Bz\cdot CHPh\cdot CN$ from $COPh\cdot CH\cdot CHPh$ and KCN is improved. $CH_2Bz\cdot CH_2\cdot CO_2H$, prepared therefrom by way of the Me ester, is reduced ($Zn-Hg-HCl$) to $Ph\cdot [CH_2]_2\cdot CHPh\cdot CO_2H$, the chloride (prep. by PCl_5) of which with $AlCl_3-C_6H_6$ gives 87% of 1-keto-2-

phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I), m.p. 76.2—77° [*semicarbazone*, m.p. 250—251.4° (decomp.; sinters at 245°)], converted by $\text{Zn-CH}_2\text{Br-CO}_2\text{Et}$ in C_6H_6 into 2-*phenyl-3 : 4-dihydro-1-naphthylacetic acid* (II), m.p. 156.2—156.8° [does not give (I) with O_3]. H_2 -Pt or -Pd, Zn-Hg-HCl, and HI-P do not affect (II), but *cis-2-phenyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid* (III), m.p. 172—172.8° (and its isomeride), is obtained in 62% yield by 2% Na-Hg in aq. EtOH if the (II) used was recovered from an unsuccessful catalytic hydrogenation, but not otherwise. With PCl_5 , followed by $\text{AlCl}_3\text{-C}_6\text{H}_6$, (III) gives *cis-8-keto-1 : 2 : 7 : 8 : 1a : 7a-hexahydrochrysene* (IV), m.p. 75.8—76.8° [*semicarbazone*, m.p. 255—258° (decomp.; sinters at 251°)], reduced (Clemmensen) to the known *cis-hexahydrochrysene*, m.p. 74.4—75.8° (Ramage *et al.*, A., 1933, 828). This proves the *cis*-structure of (III) and (IV). With MgMeBr , (IV) gives a carbinol, dehydrated at 220°, and then dehydrogenated by S at 230° to 2-methylchrysene (V) (82% yield), m.p. 161—161.4° (*picrate*, m.p. 170—170.6°). $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ then gives 2-methylchrysene-7 : 8-quinone, m.p. variable between 210—212° (decomp.) and 218—220° [not depressed by admixture with chrysene-quinone (VI)], which with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ yields a phenazine derivative, m.p. 220—221° [depressed by admixture with the phenazine derivative, m.p. 215—216°, from (VI)]. Sen-Gupta's (V) (A., 1937, II, 94; described as 6-derivative) may have been 3-methyl-1 : 2-benzanthracene. MgEtBr and (IV) yield similarly 2-ethylchrysene, m.p. 126.4—126.8° (*picrate*, m.p. 136.2—136.8°). S at 220—225° dehydrogenates (II) to 2-*phenyl-1-naphthylacetic acid*, m.p. 192—193°, which with a little ZnCl_2 in $\text{AcOH-Ac}_2\text{O}$ gives 2-chrysenyl acetate (VII), m.p. 158.6—159.2°, hydrolysed by KOH-EtOH to 2-chrysenol, m.p. 248—250° (decomp. and sinters at 240°; lit., 240—242°) [Me ether, m.p. 127.2—127.8° (lit., 126°)]. With $\text{ZnCl}_2\text{-Ac}_2\text{O-AcOH}$ (II) gives 7 : 8-dihydro-2-chrysenyl acetate, m.p. 95.6—96.2°, dehydrogenated to (VII) and hydrolysed to 7 : 8-dihydro-2-chrysenol, m.p. 156.2—156.6°. M.p. are corr. R. S. C.

Action of mixed organo-magnesium compounds on benzylimines. Preparation of secondary amines of the type $\text{CHRAr-NH-CH}_2\text{Ph}$. P. GRAMMATICAKIS (Compt. rend., 1938, 207, 1224—1225; cf. A., 1905, i, 519).—Equimol. amounts of PhCHO and $\text{CH}_2\text{Ph-NH}_2$ in C_6H_6 afford benzylidenebenzylamine, b.p. 183°/10 mm., which with MgEtBr and MgPhBr affords benzyl- α -phenylpropylamine (I), b.p. 135°/<1 mm. [*hydrochloride*, m.p. ~168° (decomp.); *nitrate*, m.p. 146°; *sulphate*, m.p. 188°; phenylcarbamyl derivative, m.p. 89°], and benzylbenzhydramine, b.p. 181°/<1 mm. [*hydrochloride*, m.p. ~230° (decomp.); *nitrate*, m.p. 206°; phenylcarbamyl, m.p. 175°, and Ac derivative, m.p. 140°], respectively. *p-Tolylidene*, b.p. 162°/<1 mm., and *p-anisylidene-benzylamine*, m.p. 40°, b.p. 204°/<1 mm., with MgEtBr afford benzyl- α -*p*-tolylpropylamine (II), b.p. 143°/<1 mm. [*hydrochloride*, m.p. ~204° (decomp.); phenylcarbamyl derivative, m.p. 100°], and benzyl- α -*p*-anisylpropylamine (III), b.p. 176°/<1 mm. [*hydrochloride*, m.p. ~191° (decomp.); *nitrate*, m.p. 129°; *sulphate*, m.p. 140°; phenyl-

carbamyl derivative, m.p. 124°], respectively. $\text{CH}_2\text{Ph-NH-CH}_2\text{Et}$ with MgPhBr , *p*- $\text{C}_6\text{H}_4\text{Me-MgBr}$, and *p*- $\text{OMe-C}_6\text{H}_4\text{-MgBr}$ affords (I), (II), and (III), respectively. J. L. D.

Action of dimethylamine on 1 : 2-dibromo-1-methylcyclohexane. J. GUTMAN (Compt. rend., 1938, 207, 1103—1104).—1 : 2-Dibromo-1-methylcyclohexane with NHMe_2 in C_6H_6 at room temp. or under pressure at 120—130° affords 2-dimethylamino-1-methyl- Δ^6 -cyclohexene (I), b.p. 85°/90 mm. (*picrate*, m.p. 162—163°; *hydrochloride*, m.p. 134—135°), which with $\text{H}_2\text{-Ni-Cr}$ gives *cis*- (II) (*picrate*, m.p. 218°) and *trans*-2-dimethylamino-1-methylcyclohexane (*picrate*, m.p. 156°). Electrolytic reduction of 2-methyl- Δ^2 -cyclohexenoneoxime in H_2SO_4 affords a mixture of 2-amino-1-methyl- Δ^6 -cyclohexene and *cis*-2-amino-1-methylcyclohexane which when methylated affords (I) and (II). J. L. D.

Sulphanilamide.—See B., 1939, 101.

Ethylenic isomerisation. IV. Stereoisomeric and chromoisomeric nitro- and amino-stilbenes. C. WEYGAND and R. GABLER (Ber., 1938, 71, [B], 2474—2478).—Decarboxylation of $\text{p-NO}_2\text{-C}_6\text{H}_4\text{-CH:CPH-CO}_2\text{H}$ in quinoline containing Cu chromite at 230° gave, in a first instance, yellow *cis-p*-nitrostilbene (I), m.p. 65°. Three successive repetitions of the experiment, in which a possibly less highly purified quinoline was used, gave a red modification (II), m.p. 65° to a yellow liquid. (II) gives a pure yellow solution in light petroleum, Et_2O , COMe_2 , or C_6H_6 and an orange solution in EtOH or CHCl_3 . Irradiation of (II) as solid or in C_6H_6 causes a rapid and extensive isomerisation to the yellow *trans*-form. When isomerised by I in PhNO_2 at 200—210° (I) gives a yellow (III) and (II) affords (III) and a green (IV) *trans-p*-nitrostilbene, both of m.p. 155—156°, but giving solutions of different colour and having different solubilities. (III) and (IV) behave as true chemical isomerides rather than as chromoisomerides. A solution of (IV) in C_6H_6 becomes brownish-yellow when irradiated and leaves (III) when the solvent is removed. Solid (IV) is unchanged by light. Reduction of (I) or (II) by $\text{FeSO}_4\text{-NH}_3$ gives *cis-p*-aminostilbene (V), b.p. 147—150°/0.2 mm., isomerised by I in C_6H_6 into the *trans*-compound (VI). (V) and (VI) are condensed with 1 : 4-OEt-C₁₀H₆-CHO to the corresponding Schiff's bases; only that derived from (VI) gives a cryst. liquid phase, thereby establishing its *trans*-structure. H. W.

Nitrosation of primary aromatic amines. L. BLANGEY (Helv. Chim. Acta, 1938, 21, 1579—1608).— NH_2Ar which do not contain strongly negative substituents are not usually diazotised by $\text{NO-SO}_3\text{H}$ in conc. H_2SO_4 . Those which couple directly with N_2 -compounds to *p*-aminoazo-dyes are usually converted into *p*-nitrosoamines. The corresponding *sec*-amines (e.g., $\alpha\text{-C}_{10}\text{H}_7\text{-NH-Et}$) can be nitrosated in the nucleus in this manner. Addition of NaNO_2 to conc. H_2SO_4 at $>10^\circ$ followed by heating of the mixture to 60°, cooling to 0—5°, and addition of $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$ in CO_2 gives mainly 4-nitroso- α -naphthylamine (I), not quite pure, m.p. ~144—145° (decomp.), with 4 : 4'-di-

amino-1:1'-dinaphthyl and possibly $(\text{NH}_2)_2$ -derivatives of 1:2'- or 2:2'-dinaphthyl. (I) is characterised by its reduction to 1:4- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ and by the hydrolysis (dil. NaOH) of its salts to 4:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$. 1:6- and 1:7- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ similarly yield the corresponding 4-NO-derivatives, converted by boiling H_2O into the respective $\text{NO}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$ and reduced to 1:4:6- $(\text{NH}_2)_2\text{C}_{10}\text{H}_5\cdot\text{SO}_3\text{H}$. 1:2- and 1:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ react similarly but less smoothly since the former undergoes more marked oxidation to naphthidine-3:3'-disulphonic acid and the latter is diazotised (on dilution) to some extent. 1:3- and 1:5- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ are not nitrosated but are diazotised to some extent. 1:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ loses SO_3H and gives 4:1- $\text{NO}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ in good yield. $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ is neither nitrosated nor diazotised and the gradual consumption of $\text{NO}\cdot\text{SO}_3\text{H}$ is unexplained. NH_2Ph is probably transformed into $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ which immediately undergoes further change. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ behaves similarly whereas $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ resembles $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$. Nitrosation occurs particularly smoothly with p -xylydine (from which small amounts of p -xyloquinone are formed by oxidation), $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and 2:1:4- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}$, less readily with $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and 3:1:4- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe}$. $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ appears to afford a NO-derivative. 2:1:4- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$ is smoothly diazotised without giving a trace of NO-derivative. The mechanism of the reaction is not elucidated but an intermediate production of $N\text{-NO}$ -derivatives is excluded.

H. W.

Action of ammonia and aromatic amines on ω -nitro-4-methylstyrene and related compounds. D. E. WORRALL (J. Amer. Chem. Soc., 1938, 60, 2841—2844).—Alkyl in the ring of ω -nitrostyrenes prevents addition of NH_3 or primary bases (A), but does not stop polymerisation. Alkyl or halogen in the side-chain hinders addition and stops polymerisation. Ph in the side-chain stops both reactions. NO_2 in the ring partly restores ability for addition without affecting polymerisation. ω -Nitro- p -methylstyrene (I), m.p. 102° (from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, MeNO_2 , and $\text{C}_6\text{H}_{11}\cdot\text{NH}_2$), with NH_3 or (A) in warm EtOH gives a polymeride, decomp. $>230^\circ$, but does not react in dry C_6H_6 ; with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in warm EtOH (not in C_6H_6) it gives the Schiff base, $\text{C}_{22}\text{H}_{20}\text{N}_2$, m.p. $188\text{--}189^\circ$ (owing to hydrolysis), and with $\text{C}_6\text{H}_{11}\cdot\text{NH}_2$ alone it gives a tar, containing $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{NC}_6\text{H}_{11}$ and MeNO_2 . The dibromide, m.p. $79\text{--}80^\circ$, of (I) is converted by $\text{KOAc}\text{-EtOH}$ into (?) ω -bromo- ω -nitro- p -methylstyrene (II), m.p. $67\text{--}67.5^\circ$ (2-, m.p. $82\text{--}83^\circ$, and 3- NO_2 -, m.p. 105° , derivatives); the corresponding (?) ω -Cl-compound, m.p. $78\text{--}78.5^\circ$ (3- NO_2 -derivative, m.p. $107\text{--}108^\circ$), is similarly prepared. With fuming HNO_3 at $<20^\circ$ (I) gives 3: ω - (III), m.p. $121\text{--}122^\circ$ (lit., $117\text{--}118^\circ$), and 2: ω -dinitro-4-methylstyrene, m.p. $96\text{--}97^\circ$. With NH_2Ph or $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in EtOH (III) gives β -nitro- α -anilino-, m.p. $98\text{--}99^\circ$, or α - p -toluidino- α -2-nitro- p -tolylethane, m.p. $135\text{--}136^\circ$ (decomp.), respectively; $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives NN' -di-(β -nitro- α -2-nitro- p -tolylethyl)- p -phenylenediamine, m.p. $152\text{--}153^\circ$ (decomp.). With NH_3 in dry C_6H_6 (III) gives di-(2: β -dinitro- α - p -tolylethyl)amine, m.p. 147° (decomp.). β -Nitro- α - p -tolyl- Δ^c -propene [prep.

using EtNO_2 as (I)], m.p. 55° , is nitrated to β :2-dinitro- α - p -tolyl- Δ^c -propene, m.p. $72\text{--}73^\circ$, which with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ affords β -nitro- α - p -toluidino- α -2-nitro- p -tolylpropane, m.p. $109\text{--}110^\circ$ (decomp.), and with $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives a product, m.p. $254\text{--}255^\circ$, stable to alkali. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CPh}\cdot\text{NO}_2$ (?) and $\text{NH}_3\text{-EtOH}$ followed by hydrolysis (HCl) give 3:5-diphenyl-4- p -tolylisooxazolone oxide (IV), m.p. $171\text{--}172^\circ$ (converted by $\text{KOH}\text{-EtOH}$ into the isooxazole, m.p. 198°), and a small amount of dibenzoyl- p -tolylmethane monooxime, m.p. $160\text{--}161^\circ$. With $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot\text{NO}_2$ and NH_3 in EtOH, (IV) yields 3-phenyl-5- p -bromophenyl-4- p -tolylisooxazolone oxide, m.p. $182\text{--}183^\circ$, and thence the derived isooxazole, m.p. 175° . R. S. C.

Action of p -toluidine and p -phenylenediamine on substituted nitrostyrenes. D. E. WORRALL and F. BENINGTON (J. Amer. Chem. Soc., 1938, 60, 2844—2845).—OH, OMe, or CH_2O_2 in the ring stops reaction of ω -nitrostyrenes with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ or $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (I), unless (sometimes) NO_2 is also present. Halogen in the ring also aids addition. ω -Nitro- o -methoxystyrene (obtained from $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, MeNO_2 , and NET_3 in EtOH), m.p. 50° , with fuming HNO_3 gives α :4-dinitro- β - o -anisylethylene, m.p. $175\text{--}176^\circ$. α :2-Dinitro- β - p -anisylethylene, m.p. $145\text{--}146^\circ$, is similarly prepared. Condensation with (I) yields NN' -di-(β -nitro- α - o -, m.p. 147° , α - m -, m.p. 168° , and α - p -nitro-, m.p. 172° , α -4-nitro-2-methoxy-, m.p. $157\text{--}158^\circ$, and α -4-chloro-2-nitro-phenylethyl)- p -phenylenediamine, m.p. $156\text{--}157^\circ$. β -Nitro- α - p -toluidino- α -4-chloro-2-nitro-phenylethane, m.p. $136\text{--}137^\circ$ (decomp.), is also prepared. R. S. C.

Action of aromatic amines on 2-chloro-4: ω -dinitrostyrene. D. E. WORRALL (J. Amer. Chem. Soc., 1938, 60, 2845—2846).—4:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$ adds bases more readily than does the 2:4:1-isomeride; in many cases it is more reactive than is $\text{CHPh}\cdot\text{CH}\cdot\text{NO}_2$, but the oxidising effect due to the NO_2 -groups prevents reaction with NH_2Ph or $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NH}_2$, causes tars to be formed with N_2H_4 or NH_2OH , and leads to destruction of the NH_3 -addition product by EtOH. o -Chloro- ω -nitrostyrene (prep. by use of NET_3), m.p. 48° , gives 2-chloro-4: ω -dinitrostyrene, m.p. $149\text{--}150^\circ$; addition of Br and subsequent elimination of HBr by $\text{KOAc}\text{-EtOH}$ converts these compounds into α -bromo- α -nitro- β - o -chloro-, m.p. $132\text{--}133^\circ$, and β -2-chloro-4-nitro-phenylethylene, m.p. $60\text{--}61^\circ$, respectively. Condensation with the appropriate base leads to α -nitro- β - o -, m.p. $117\text{--}118^\circ$, α - m -, m.p. $127\text{--}128^\circ$, and α - p -toluidino-, m.p. $130\text{--}131^\circ$, β - p -anisidino-, m.p. $88\text{--}89^\circ$, β -phenylhydrazino-, m.p. $133\text{--}134^\circ$, and β - p -tolylhydrazino-, m.p. $127\text{--}128^\circ$, β -2-chloro-4-nitrophenylethane, α -bromo- α -nitro- β - p -toluidino- β -2-chloro-4-nitrophenylethane, m.p. 138° (decomp.), NN' -di-(β -nitro- α - o -chlorophenylethyl)- p -phenylenediamine, m.p. $147\text{--}148^\circ$ (decomp.), di-(β -nitro- α -2-chloro-4-nitrophenylethyl)amine, m.p. $118\text{--}119^\circ$, and NN' -di-(β -nitro- α -2-chloro-4-nitrophenylethyl)- p -phenylenediamine, m.p. $201\text{--}202^\circ$, and benzidine, m.p. $137\text{--}138^\circ$. R. S. C.

Structure and mechanism of formation of the Bandrowski base. W. M. LAUER and C. J. SUNDE

(J. Org. Chem., 1938, 3, 261—264).—Bandrowski's base (A., 1894, i, 236), prepared by oxidation of p - $C_6H_4(NH_2)_2$, is 2 : 5-di-(p -aminoanilo)-1 : 4-phenylenediamine (cf. Green, J.C.S., 1913, 103, 933), because with hot 10% HCl it gives 1.74 mols. of p - $C_6H_4(NH_2)_2$ and because its diacetate, m.p. 310—311° (converted by Ac_2O at 100° into the known tetra-acetate), is obtained from p - $C_6H_4(NH_2)_2$ and p - NH_2 - C_6H_4 -NHAc (best 0.66 mol.) in H_2O or H_2O -MeOH- Et_2O -HCl at 0°. It is held to be formed by addition to give 2 : 1 : 4-(p -NHAc- C_6H_4 -NH)- $C_6H_3(NH_2)_2$, oxidation thereof to the di-imine, and further addition; formation of the base from p - $C_6H_4(NH_2)_2$ follows a similar route. R. S. C.

Stability of dithizone solutions.—See A., 1939, I, 98.

Synthesis of dinaphthylthiocarbazone, and formation of its intra-complex salts with heavy metals. I. B. SUPRUNOVITSCH (J. Gen. Chem. Russ., 1938, 8, 839—843).—Naphthylhydrazine naphthylthiocarbazinate heated in CO_2 at 135° yields dinaphthylthiocarbazide, which with 5% KOH in EtOH gives the K salt of dinaphthylthiocarbazone (I). Solutions of (I) in COMe₂ give coloured ppts. with heavy metals (Cu, Ag, Au, Zn, Cd, Hg, Pb, Mn, Co, Ni); 0.06 µg. of Pb in 1 ml. of solution may be thus detected, as compared with 3 µg. with dithizone. R. T.

Diazotation, decomposition of diazo-compounds, and coupling of isomeric xylylides with p -nitrobenzenediazonium salts. V. R. FEDOROV, A. A. SPRISKOV, and E. I. SCHELUDJAKOVA (J. Gen. Chem. Russ., 1938, 8, 844—850).—The velocity of diazotation at 0° rises in the series 1 : 3 : 4- < 1 : 2 : 4- < 1 : 4 : 2- $C_6H_3Me_2$ -NH₂; that of 1 : 3 : 2- $C_6H_3Me_2$ -NH₂ could not be measured, owing to decomp. of the diazonium salt at 0°. The velocity of decomp. of the diazo-compounds at 40° rises in the order 1 : 3 : 4- < 1 : 2 : 4- < 1 : 3 : 2- < 1 : 4 : 2- $C_6H_3Me_2$ -NH₂. 1 : 3 : 2- and 1 : 4 : 2-, but not 1 : 3 : 4- and 1 : 2 : 4- $C_6H_3Me_2$ -NH₂, can be coupled with p -NO₂- C_6H_4 -N₂Cl in HCl at 18°. R. T.

Condensation of phenols with formaldehyde. E. BUREŠ and A. MASÁREK (Časopis českoslov. Lék., 1936, 16, 177—188; Chem. Zentr., 1937, i, 1291).—The rate of reaction of the following ArOH (mol. amounts) with 40% CH₂O at 100° (bath) in presence of 1% of catalyst is: m - > o -cresol = PhOH (technical > pure) > p -cresol. The strongest bases and acids are the most active catalysts. PhOH and 40% CH₂O at 100° (bath)/50 hr. in absence of catalyst give resinous material from which H_2O extracts 2 : 4'-(I) (dibenzoate, m.p. 115°) and 4 : 4'-dihydroxydiphenylmethane (II) [dibenzoate, m.p. 156°; compound, m.p. 150° (decomp.)], with $(CH_2)_6N_4$ and o -OH- C_6H_4 -CH₂-OH. (II) reacts slowly and (I) somewhat more quickly with CH₂O; alkaline catalysts lead to resins. Oxidation (air; alkaline KMnO₄) of (I), (II), and products therefrom (all of which couple with p -NO₂- C_6H_4 -N₂Cl) gives brown, amorphous, alkali-sol. material. Nitration (method: Staedel, A., 1895, i, 232) of CH₂Ph₂ gives the 2 : 4'- and (mainly) 4 : 4'-(NO₂)₂-derivatives; the respective (NH₂)₂-compounds are converted (diazo-method) into (I) and (II).

Saturated solutions of PhOH and $(CH_2)_6N_4$ in H_2O and EtOH afford the compounds, $(CH_2)_6N_4$ ·3PhOH, m.p. 124° (decomp.), and $(CH_2)_6N_4$ ·PhOH, m.p. 176.5° (decomp.), respectively; in COMe₂, cryst. compounds, m.p. 80°, 112°, 125°, and 160—161°, are formed. H. B.

Action of gaseous hydrogen chloride on 4-nitroso- α -naphthol and 4-nitrosoguaiacol. A. ANGELETTI and M. PIRONA (Atti R. Accad. Sci. Torino, Cl. Sci. fis. mat. nat., 1936, 71, I, 602—606; Chem. Zentr., 1937, i, 1138).—4 : 1-NO- $C_{10}H_6$ -OH (reacting as quinoneoxime) in cold Et_2O saturated with dry HCl gives NH₂OH and 2 : 3-dichloro-1 : 4-naphthaquinone. 4-Nitrosoguaiacol (OH = 1), however, similarly yields 3-chloro-4-nitrosoguaiacol (I), decomp. 255° (darkens 213°), and an amorphous violet substance, but no NH₂OH. Reduction (SnCl₂, conc. HCl) of (I) affords the 4-NH₂-compound, decomp. 160° (darkens 154°), the diazonium salt of which with cold conc. NaOH gives 3-chloroguaiacol, m.p. 32—33°. H. B.

Synthesis of derivatives of quinol related to dihydroflavoglaucin. J. H. CRUICKSHANK and R. ROBINSON (J.C.S., 1938, 2064—2071).—Bu^oCOCl and p -OMe- C_6H_4 -OH- C_5H_5 -N- Et_2O give p -anisyl valerate, b.p. 150—152°/10 mm., converted by AlCl₃ at 100° (bath) into 2-hydroxy-5-methoxy- n -valerophenone (I), m.p. 62° (2 : 4-dinitrophenylhydrazone, m.p. 186°), also obtained from Bu^oCOCl-AlCl₃-CS₂ and p - C_6H_4 (OMe)₂-CS₂. (I) and Zn-Hg in 20% HCl, boiled for 4 hr., afford 2-hydroxy-5-methoxy- n -amylbenzene (II), m.p. 44°, which with n -octoyl chloride (III) in C_5H_5 -N- Et_2O gives 4-methoxy-2- n -amylphenyl octoate, b.p. 167—171°/0.1 mm. This and AlCl₃ in H_2 at 100° (bath) afford 2-hydroxy-5-methoxy-3- n -amylcyclohexenone, b.p. 180—190°/0.1 mm. (2 : 4-dinitrophenylhydrazone, m.p. 103°), attempted demethylation (AlBr₃, HBr, HI) of which gives only n -amylquinol. (II) and Me₂SO₄-20% NaOH-COMe₂ yield 2 : 5-dimethoxy- n -amylbenzene, b.p. 144—146°/12 mm., which with (III) and AlCl₃-CS₂ first at 0° and finally at the b.p. gives 2-hydroxy-5-methoxy-4- n -amylcyclohexenone (IV), m.p. 42° (2 : 4-dinitrophenylhydrazone, m.p. 117°), demethylated readily by AlBr₃- C_6H_6 to the 2 : 5-(OH)₂-derivative, m.p. 94° (2 : 4-dinitrophenylhydrazone, m.p. 112°). Successive reduction (Clemmensen), methylation (Me₂SO₄), and oxidation (AcOH-HNO₃) of (IV) gives 2- n -amyl-5- n -octyl- p -benzoquinone (V), m.p. 65°. The corresponding quinol is prepared from (V) and EtOH-Na₂S₂O₄. Quinol and Bu^oCOCl in C_5H_5 -N- Et_2O at 0°—room temp., give quinol diisovalerate, m.p. 55°, which with quinol and AlCl₃ at 150—160° affords 2 : 5-dihydroxyisovalerophenone, m.p. 110°. The latter and CH₂PhCl-NaOEt-EtOH at 100° (bath) give 2-hydroxy-5-benzoyloxyisovalerophenone, m.p. 60° (NH₂-NH-CO-NH₂, HCl- C_5H_5 -N or excess of N₂H₄, H_2O -AcOH gives the ketazine, m.p. 174°). p - C_6H_4 (OMe)₂ and Bu^oCOCl with AlCl₃-CS₂ afford 2-hydroxy-5-methoxy- [semicarbazone (VI), m.p. 171°] and 2 : 5-dimethoxy-isovalerophenone (VII), b.p. 124—126°/1 mm. The latter is prepared pure from the crude reaction product and Me₂SO₄-10% NaOH-COMe₂. (VI) and NaOEt-EtOH at 180—185° give the corresponding ketazine, m.p. 144°. (VII) is

reduced (Clemmensen) to 2:5-dimethoxyisoamylbenzene, b.p. 100–102°/2 mm., converted by (III) and $\text{AlCl}_3\text{-CS}_2$ into 2-hydroxy-5-methoxy-4-isoamyl-octophenone (2:4-dinitrophenylhydrazones, m.p. 146°). Heating of 2-hydroxy-5-allyloxyacetophenone, b.p. 123–125°/2 mm. (cf. Baker *et al.*, A., 1936, 474), gives 2:5-dihydroxy-6-allylacetophenone, which with H_2 (2–3 atm.) and Pd-SrCO_3 in EtOAc affords 2:5-dihydroxy-6-*n*-propylacetophenone (+ H_2O), m.p. 88°, the CO of which is inert. 2:5-Dimethoxy-6-allyl-phenyl styryl ketone and KMnO_4 in boiling aq. NaOH give 3:6-dimethoxyphthalic anhydride. EtCOCl and $p\text{-C}_6\text{H}_4(\text{OMe})_2$ give (Friedel-Crafts) an oil, reduced (Clemmensen) to 2:5-dihydroxy-*n*-propylbenzene, m.p. 87°; the corresponding 2:5-(OMe)₂-compound, b.p. 128–130°/20 mm. (NO_2 -derivative, m.p. 64°), with $\text{AcCl-AlCl}_3\text{-CS}_2$ at 0°–100° (bath) gives 2-hydroxy-5-methoxy-4-*n*-propylacetophenone, b.p. 150–155°/1 mm., which with $\text{AlBr}_3\text{-C}_6\text{H}_6$ affords the corresponding 2:5-(OH)₂-compound, m.p. 85° (2:4-dinitrophenylhydrazones, m.p. 216°), and *n*-propylquinol. $p\text{-C}_6\text{H}_4(\text{OMe})_2$ and (III) in $\text{CS}_2\text{-AlCl}_3$ at 0–100° (bath) afford 2-hydroxy-5-methoxyoctophenone, m.p. 45° (2:4-dinitrophenylhydrazones, m.p. 134°), demethylated by $\text{AlBr}_3\text{-C}_6\text{H}_6$ to the 2:5-(OH)₂-compound (VIII), m.p. 86° (2:4-dinitrophenylhydrazones, m.p. 186°), converted by *n*-amyl bromide and NaOEt-EtOH into 2-hydroxy-5-*n*-amyl-octophenone, b.p. 190–195°/1.5 mm. (2:4-dinitrophenylhydrazones, m.p. 121°); the latter and $\text{AlCl}_3\text{-CS}_2$ at room temp. for 3 days give (VIII). A. T. P.

Synthesis of $\alpha\beta$ -dichloro- α -*p*-anisylethane; conversion into β - and α -chloro- α -*p*-anisylethylene. R. QUELET and J. ALLARD (Compt. rend., 1938, 207, 1109–1111; cf. A., 1936, 719).— PhOMe with $\text{CH}_2\text{Cl-CH(OEt)}_2$ in conc. HCl saturated with HCl at 70° affords $\alpha\beta$ -dichloro- α -*p*-anisylethane (I) and β -chloro- α -di-*p*-anisylethane (II). The crude prep. when rapidly distilled at 100° (bath)/vac. and then treated with $\text{C}_2\text{H}_5\text{N}$ at 115° affords β -chloro- α -*p*-anisylethylene [from (I)] and *s*-di-*p*-anisylethylene [from (II)]; with NaOEt or KOH-EtOH mainly α -chloro- α -*p*-anisylethylene (III), m.p. 35°, and some α -di-*p*-anisylethylene result. (III) is easily hydrolysed to $p\text{-OMe-C}_6\text{H}_4\text{-COMe}$ and readily oxidises in air to a red substance. J. L. D.

Natural ethers of phenols with prenologous alcohols. VIII. Constitution and synthesis of foeniculin. E. SPÄTH and J. BRUCK (Ber., 1938, 71, [B], 2708–2711).—The occurrence of the residues $\text{CMe}_2\text{:CH-CH}_2\text{}$ (I), $\text{CMe}_2\text{:CH-CH}_2\text{-CH}_2\text{-CMe:CH-CH}_2\text{}$, and $\text{Me[CMe:CH-CH}_2\text{-CH}_2\text{]}_2\text{-CMe:CH-CH}_2\text{}$ as side-chains of natural coumarins is noted and for (I) the name “prenyl” is suggested to indicate the close relationship to isoprene. Foeniculin (II), b.p. 147°/5 mm., m.p. (vac.) 23.5–24.5°, obtained by Takens (B., 1929, 910) from fennel and star anise oils, is $\text{C}_{14}\text{H}_{18}\text{O}$. It passes at 260° into *p*-anol ($p\text{-OH-C}_6\text{H}_4\text{:CH:CHMe}$) (III). It is hydrogenated (Pd sponge in MeOH) to tetrahydrofoeniculin, b.p. 100–110° (bath)/0.03 mm., converted by distillation with HI (*d* 1.7) into dihydro-*p*-anol ($p\text{-C}_6\text{H}_4\text{Pr}^{\text{OH}}$) and isoamyl iodide. (II) is $p\text{-}\Delta^{\alpha}\text{-propenylphenyl } \gamma\text{-methyl-}\Delta^{\beta}\text{-butenyl ether}$ since it is obtained from (III) and D (A., II.)

$\text{CMe}_2\text{:CH-CH}_2\text{Br}$. The ready hydrolysis of (II) by AcOH containing a little conc. H_2SO_4 is remarkable as is its instability to heat, whereby either migration of the prenyl residue from O to C occurs or elimination of isoprene is observed. H. W.

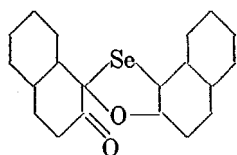
Mechanism of rearrangement of phenyl ethers. W. J. HICKINBOTTOM (Nature, 1938, 142, 830).—The migration of R (= CH_2Ph , allyl, *tert*-alkyl) from O to the nucleus which occurs when PhOR are heated at the b.p., and its transference to a suitable solvent can be explained by assuming that R is first eliminated as a free radical. L. S. T.

Identification of naphthyl ethers as picrates. V. H. DERMER and O. C. DERMER (J. Org. Chem., 1938, 3, 289–293).—The following, prepared from $\text{C}_{10}\text{H}_7\text{-OH}$, ROH , and H_2SO_4 , or $\text{C}_{10}\text{H}_7\text{-ONa}$ and RAl in EtOH , are purified by way of the picrates, the m.p. of which are given in parentheses (italics for new picrates). $\alpha\text{-C}_{10}\text{H}_7$, Me, b.p. 271° (129.5–130.5°), Et, b.p. 280.5° (118.5–119°), Pr^{β} , b.p. 282.5° (104.5–105.5°), Pr^{α} , b.p. 293.5° (99.5–100°), CHMeEt , b.p. 293.5° (100.5–101°), Bu^{β} , b.p. 301.5° (104.5–105.5°), Bu^{α} , b.p. 308.5° (85°), isoamyl, b.p. 317.5° (96–97°), *n*-amyl, b.p. 322°, m.p. 30° (75–75.5°), CH_2Ph , m.p. 77–77.5° (decomp. 85–100°), $\text{CH}_2\text{Ph-CH}_2$, m.p. 72–72.5° (117.5–118.5°), and allyl (100.5–101°) ether; $\beta\text{-C}_{10}\text{H}_7$, Me, b.p. 273°, m.p. 72.5–73° (116.5–117°), Et, b.p. 282°, m.p. 35.5–36° (101–101.5°), Pr^{β} , b.p. 285°, m.p. 40° (95–95.5°), Pr^{α} , b.p. 297°, m.p. 39.5–40° (80.5–81.5°), CHMeEt , b.p. 298.5° (86–86.5°), Bu^{β} , b.p. 304.5°, m.p. 33–33.5° (84–85°), Bu^{α} , b.p. 309° (67–67.5°), isoamyl, b.p. 321°, m.p. 28–28.5° (93.5–94°), *n*-amyl, b.p. 327.5°, m.p. 24.5° (66.5–67°), CH_2Ph , m.p. 101.5–102° (123°), $\text{CH}_2\text{Ph-CH}_2$, m.p. 70–70.5° [83–84° (sinters and turns red at 67.5°)], and allyl, m.p. 16° (98.5–99°), ether. Di- β -naphthyl methylene and ethylene ethers give no picrates. M.p., if not given, are <–10°. The picrates give satisfactory mixed m.p. depressions. Temp. are corr. R. S. C.

Derivatives of *o*-aminophenol. II. L. GALATIS (J. pr. Chem., 1938, [ii], 151, 331–341; cf. A., 1934, 183).—*N*-Acetyl-2-phenylbenzoxazoline (*loc. cit.*) with conc. HCl at room temp. gives 3:3'-diacetamido-4:4'-dihydroxytriphenylmethane (I), m.p. ~265° (decomp.) after darkening, which rapidly darkens on exposure to air; under precisely similar conditions it is obtained from $o\text{-NHAc-C}_6\text{H}_4\text{-OH}$ and PhCHO . (I) is transformed by hot Ac_2O containing a little conc. H_2SO_4 into its diacetate, m.p. 240°, and by $\text{Me}_2\text{SO-10\% NaOH}$ into the Me_4 derivative, $\text{C}_{27}\text{H}_{30}\text{O}_4\text{N}_2$, m.p. 220°. Boiling 20% HCl hydrolyses (I) to the 3:3'-(NH_2)₂-derivative, m.p. 193°. The presence of *p*-OH in (I) is established by the production of a dye when (I) is oxidised. H. W.

Covalent alkaline derivatives of di-2-hydroxy-1-naphthyl selenide and allied substances. V. DVORKOVITZ and S. SMILES (J.C.S., 1938, 2022–2028; cf. A., 1937, II, 336).—Di-2-hydroxy-1-naphthyl selenide (I) [*Me ether*, m.p. 148°, from (II) (below) and $\text{MeOH-Me}_2\text{SO}_4$ at 35°] and *n*- NaOH (2 mols.) afford the yellow *Na* derivative (II) (+ $4\text{H}_2\text{O}$), m.p. 270° (previous loss of H_2O); boiling CHCl_3 then gives the

colourless anhyd. *Na* salt, no m.p. KOH and LiOH similarly afford a yellow *K* derivative (which when dried at 15° forms a paler *dihydrate*, m.p. 170°), and a *Li* derivative (+4H₂O), no m.p., respectively. (I)



(A.)

(1 mol.) and K₃Fe(CN)₆ (2.2 mols.) in aq. KOH afford the *dehydro-selenide* (A), m.p. 145°. (I) or the corresponding sulphide forms unstable Cu derivatives. Covalent mono-alkali derivatives could not be obtained from di-2-hydroxy-1-naphthyl sulphoxide, sulphone, or disulphide (cf. *loc. cit.*). Di-2-chloro-5-hydroxy-*m*-4-xylyl sulphide (III) similarly gives *Na* (+2H₂O), *K* (+2H₂O), and *Li* (+2H₂O) derivatives; (III) and hot 1.5% aq. NaOH (1.1 mols.) afford an "acid" *Na* salt, C₁₆H₁₅O₂Cl₂SN_a, C₁₆H₁₆O₂Cl₂S. Under similar conditions, di-2-hydroxy-1-naphthyl sulphide (IV) or -naphthylmethane give the normal *Na* derivatives (+4H₂O), but (IV) and hot aq. KOH (1.2 mols.) give the *acid K* salt (+2H₂O), m.p. 200°. Di-6-chloro-3-hydroxy-2-*p*-xylyl sulphide affords *Na* (+4H₂O, m.p. 255°; +2H₂O, m.p. 255°, and anhyd.), *K* (+2H₂O), m.p. 260°, and *Li* derivatives (+4H₂O, m.p. 200°; converted in N₂ at 26° into the *dihydrate*). Di-5-hydroxy-6-*ψ*-cumyl sulphide similarly affords *Na* [+4H₂O, m.p. 245° (previous loss of H₂O), and +2H₂O], *Li* (+4H₂O and +2H₂O, m.p. ~150°), and an *acid K* salt (+2H₂O), m.p. 223°. The *Li* derivative (+4H₂O) of di-5-hydroxy-6-*ψ*-cumylmethane is more stable than that of the sulphide. Di-6-chloro-3-hydroxy-2-cymyl sulphide affords *Na* (+2H₂O, m.p. 125°; unstable tetrahydrate), *K* (+2H₂O), m.p. 206°, and *Li* (+2H₂O), m.p. 95°, derivatives. 5-Chloro-*o*-4-xylenol and S₂Cl₂-AlCl₃-CS₂ for 24 hr. at 16° afford *di*-5-chloro-4-hydroxy-*o*-3-xylyl sulphide, m.p. 154° [*Na* derivative (+4H₂O)], converted by 2% aq. NaOCl-NaOH into the *dehydro*-derivative, m.p. ~115°. *o*-4-Xylenol and S₂Cl₂-CHCl₃ give *di*-4-hydroxy-*o*-5-xylyl sulphide, m.p. 157°, converted by SO₂Cl₂ in CHCl₃ at 15° into *di*-3-chloro-4-hydroxy-*o*-5-xylyl sulphide, m.p. 145°; neither sulphide affords a covalent *Na* or *dehydro*-derivative. *m*-5-Xylenol and S₂Cl₂-CHCl₃ give *di*-5-hydroxy-*m*-2-xylyl sulphide, m.p. 265°, and *m*-6-xylyl sulphide, m.p. 149° (*acid Na* salt). Salicylideneacetophenone (1 mol.) also affords covalent *Na* (+2H₂O) (1:1 adduct with salicylaldehyde; the *Na* derivative of *p*-hydroxybenzylideneacetophenone does not yield an analogous adduct), *K* (+2H₂O), m.p. 175°, and *Li* (+2H₂O), m.p. 250° (decomp.), derivatives. Salicylideneacetone and NaOEt-EtOH-Et₂O afford the *Na* salt (+4H₂O) (1:1 adduct with salicylaldehyde). 2-Salicylidene-5-methylcyclohexanone affords *Na* (+4H₂O), m.p. 190° (after loss of some H₂O), *K* (+2H₂O), m.p. ~95° (also +2H₂O), and *Li* (+4H₂O) derivatives, m.p. ~235°.

A. T. P.

Diene syntheses. X. Diene syntheses with αβ-unsaturated nitro-derivatives, sulphones, and thioethers. K. ALDER, H. F. RICKERT, and E. WINDEMUTH (Ber., 1938, 71, [B], 2451—2461).—CH₂:CH·NO₂ behaves in diene additions in the same manner as CH₂:CH·CHO or CH₂:CH·CO₂H giving with cyclopentadiene (I), in abs. Et₂O at 105—110°,

2-nitronorbornylene, hydrogenated (PtO₂ in AcOH) to 2-nitronorbornylene, which is reduced (Fe powder) to endonorbornylamine. Similarly (I) and CHMe:CH·NO₂ in AcOH at 103° afford 2-nitro-3-methyl-Δ⁵-norbornylene, b.p. 94—95°/14 mm., whence 2-nitro-, b.p. 101—102°/15 mm., 2-amino- (hydrochloride, m.p. 269°; picrate, m.p. 202—203°), and 2-carbamido-3-methylnorbornylene, m.p. 203°. α-Nitro-Δ^α-pentene (II) yields successively 2-nitro-3-*n*-propyl-Δ⁵-norbornylene, b.p. 122—125°/14 mm., norbornylene, b.p. 126°/14 mm., and 2-amino-3-*n*-propyl-norbornylene (hydrochloride, m.p. 223°; picrate, m.p. 176°). 1-Nitro-2-*n*-propyl-Δ⁴-cyclohexene, b.p. 118°/11 mm., is derived from (II) and (CH₂:CH)₂ (III) containing a little quinol at 100—110°, whilst (CH₂:CMe)₂ (IV) affords 1-nitro-4:5-dimethyl-2-*n*-propyl-Δ⁴-cyclohexene, b.p. 146—147°/12 mm. αβ-Unsaturated sulphones at 140—150° add dienes according to the scheme of a diene synthesis. Thus *p*-tolyl vinyl sulphone and (IV) give 3:4-dimethyl-Δ³-cyclohexenyl *p*-tolyl sulphone, m.p. 82—83°. Δ²-Butadienesulphone (V) is transformed by (III) into 1:2:3:6:7:8-hexahydrothionaphthensulphone, b.p. 131—133°/0.1 mm., m.p. 94—95°, by (IV) into 4:5-dimethyl-1:2:3:6:7:8-hexahydrothionaphthensulphone, m.p. 96°, and by (I) into 3:6-endomethylene-1:2:3:6:7:8-hexahydrothionaphthensulphone (VI), m.p. 141—142°, with the compound, C₁₄H₁₈O₂S, m.p. 218°, formed from 2 mols. of (I) and one of (V). PhN₃ and (VI) give isomeric hydrotriazoles, C₁₅H₁₇O₂N₃S, m.p. 187—188° and 200° (decomp.). *p*-C₆H₄Me·S·CH₂CH₂ and (I) at 180—190° yield 2:5-endomethylene-Δ³-cyclohexenyl *p*-tolyl sulphide, b.p. 175—178°/11 mm.

H. W.

Magnesium pentamethylphenyl bromide. H. CLÉMENT (Compt. rend., 1938, 207, 864—866; cf. A., 1937, II, 331; 1938, II, 275).—C₆Me₅·MgBr with MeCHO, CH₂O, and EtOBz affords some pentamethylphenylmethylcarbinol, m.p. 141° (acetate, m.p. 157°), pentamethylbenzyl alcohol, m.p. 136—137°, and pentamethylbenzophenone, m.p. 125°, respectively.

J. L. D.

Reactions of epoxy-compounds with reagents.

I. Interaction of epoxyphenylethane (styrene oxide) and magnesium aryl halides. M. S. KHARASCH and H. G. CLAPP (J. Org. Chem., 1938, 3, 355—360).—Addition of epoxyphenylethane (I) to MgPhBr gives ββ-diphenylethyl alcohol (II), b.p. 125—135° (oxalate, m.p. 160.5°; 3:5-dinitrobenzoate, m.p. 135°), but addition of MgPhBr to (I) gives CH₂Ph·CHPh·OH; oxidation of the product to CPh₂ or BzOH indicates formation of a small amount of the isomeride in each case. *p*-OMe·C₆H₄·MgBr reacts similarly. (II) is synthesised by the following reactions (not detailed): OH·CH₂·CO₂Et + 3MgPhBr → C₆H₅ + OH·CPh₂·CH₂·OH (III) + EtOH + 3MgBrOH; (III) in hot 0.5N-HCl gives CHPh₂·CHO, hydrogenated (Pt) to (II). With P₂O₅ in C₆H₆, (II) gives (CHPh)₂.

R. S. C.

Synthesis of alcoholic derivatives of the fatty series. I. Catalytic hydrogenation of phenylstearic acid under pressure. W. KIMURA, T. OMURA, and H. TANIGUCHI (Ber., 1938, 71, [B], 2686—2687).—Oleic acid is converted by AlCl₃ and

C_6H_6 (free from S compounds) into α -phenylstearic acid, reduced (300—310°/25—100 atm., Cu—Cr—Ba oxide catalyst) to α -phenylstearyl alcohol, identified as the urethane. H. W.

Action of magnesium halide etherates on epoxides. M. TIFFENEAU and B. TCHOUBAR (Compt. rend., 1938, 207, 918—919).— β -Epoxy-pentane with $MgBr_2$ etherate in the cold (and decomp. with H_2O ; general method) affords a mixture, b.p. 67—68°/15 mm., of $CHMeBr \cdot CHEt \cdot OH$ and $CHEtBr \cdot CHMe \cdot OH$ (preponderates); in the hot $COEt_2$ and $COMePr^a$ (preponderates) are formed. Similarly, 1:2-epoxy-cyclohexane with $MgHal_2$ in the cold affords *trans*-2-bromo-, b.p. 90—91°/13 mm. (*p*-nitrobenzoate, m.p. 59—60°; 3:5-dinitrobenzoate, m.p. 155°), and *trans*-2-iodo-cyclohexanol, m.p. 40° (*p*-nitrobenzoate, m.p. 74—75°; 3:5-dinitrobenzoate, m.p. 157°); when it is heated, cyclopentylformaldehyde is formed. 1-Methyl-1:2-epoxycyclohexane and $MgBr_2$ in the cold yield the stable *trans*-2-bromo-1-methyl-, b.p. 100—101°/16 mm. (*p*-nitrobenzoate, m.p. 130°; 3:5-dinitrobenzoate, m.p. 120°), and *trans*-2-bromo-2-methyl-cyclohexanol which easily loses Br; in the hot cyclopentyl Me ketone (*semicarbazone*, m.p. 145°), 2-methylcyclopentylformaldehyde (*semicarbazone*, m.p. 168°), and some 2-methylcyclohexanone (*semicarbazone*, m.p. 198°) result. Methylenecyclohexane oxide with $MgBr_2$ gives 1-bromo-1-hydroxymethylcyclohexane, m.p. 82° (3:5-dinitrobenzoate, m.p. 133°) (cold), or hexahydrobenzaldehyde (hot). Styrene oxide with $MgHal_2$ (cold) forms β -bromo-, b.p. 131—132°/19 mm. (*p*-nitrobenzoate, m.p. 56—57°; 3:5-dinitrobenzoate, m.p. 103°), and β -iodo- β -phenylethyl alcohol (*p*-nitrobenzoate, m.p. 76°; 3:5-dinitrobenzoate, m.p. 110°); when this is heated $CH_2Ph \cdot CHO$ is formed. The

above results show that $CHR \cdot O \cdot CHR'$ react with, e.g., $MgBr_2$ in the cold to give $CHRBr \cdot CHR' \cdot O \cdot MgBr$ (or the isomeride); when heated, the latter loses $MgBr_2$ affording $CH_2R \cdot COR'$ (with or without transposition). J. L. D.

Catalytic hydrogenation of hydroxymethylcyclohexanone. H. RUPE and O. KLEMM (Helv. Chim. Acta, 1938, 21, 1538—1541).—Hydrogenation (Ni-aq. EtOH; atm. pressure) of hydroxymethylcyclohexanone (I) gives 2-hydroxymethylcyclohexanol (II), b.p. 135—137°/9 mm. (diacetate, b.p. 133°/13 mm.; di-*p*-nitrobenzoate, m.p. 134°). With this on a SiO_2 gel catalyst uniform products are not obtained if hydrogenation is interrupted after the absorption of 1 H_2 . Na—Hg and AcOH reduce (I) to (II) accompanied by much resin. Cu chromite appears inactive under 150 atm. Gradual addition of 20% H_2SO_4 to (II) in EtOH through which steam is passing gives the corresponding oxide, b.p. 54°/11 mm., in poor yield. H. W.

Reduction of α -halogeno-ketones. Synthesis of *dl*- β -ephedrine. P. G. STEVENS (J. Amer. Chem. Soc., 1938, 60, 3089).— $Al(OPr^a)_3$ partly removes Br in the α -position to CO if H is available on the adjacent C. $COPh \cdot CHMeBr$ and $Al(OPr^a)_3$ give only 35% of $OH \cdot CHPh \cdot CHMeBr$, b.p. 73—75°/0.1 mm., which with NH_2Me yields a mixture containing *dl*- β -ephedrine, but no *dl*-ephedrine. R. S. C.

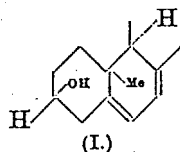
Reactions of benzhydryl chloride with hydroxylic solvents.—See A., 1939, 1, 86.

Reactivity of *p*-fluorine in triarylmethyl chlorides. F. BACON [with J. H. GARDNER] (J. Org. Chem., 1938, 3, 281—286).—*p*-F in CAr_3Cl reacts in the same way as, but less readily than, *p*-Br or *p*-Cl. *p*- $C_6H_4 \cdot F \cdot COPh$ and $MgPhBr$, followed by $HCl \cdot C_6H_6$ on the purified product, give *p*- $C_6H_4 \cdot F \cdot CPh_2Cl$ (I), m.p. 90—91° (lit., 87°). (*p*- $C_6H_4 \cdot F$) $_2CPh \cdot OH$ (from *p*- $C_6H_4 \cdot F \cdot MgBr$ and $MeOBz$) and HCl in light petroleum give *pp'*-difluorotriphenylmethyl chloride (II) (14%), m.p. 56—57°. (*p*- $C_6H_4 \cdot F$) $_3C \cdot OH$ (from *p*- $C_6H_4 \cdot F \cdot MgBr$ and *p*- $C_6H_4 \cdot F \cdot CO_2Me$) gives similarly impure *tri-p*-fluorophenylmethyl chloride (III) (4%), m.p. 81—82°. In liquid SO_2 , with or without $AgCl$, small amounts of F⁺ are formed by rearrangement of (I), (II), or (III). With Ag in C_6H_6 under CO_2 reaction to radicals of the type, *p*- $CAr_3 \cdot C_6H_4 \cdot CAr_2$, occurs slowly. R. S. C.

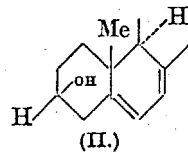
Separation of sterols by chromatographic adsorption. K. LADENBURG, E. FERNHOLZ, and E. S. WALLIS (J. Org. Chem., 1938, 3, 294—299).—Cholesteryl (I), m.p. 188—189°, stigmasteryl, m.p. 191—192°, and ergosteryl, m.p. 200—201°, azobenzene-4-carboxylate are separated by adsorption from C_6H_6 on anhyd. Al_2O_3 and development of the chromatogram by light petroleum or, less well, a mixture thereof with C_6H_6 . Presence of the β -sitosteryl ester (II), m.p. 173—174°, prevents the separation, although some pure (II) is obtained from the portion least adsorbed unless (I) is also present. *p*- $COCl \cdot C_6H_4 \cdot N \cdot NPh$, m.p. 93—94°, is obtained from the acid by $SOCl_2$ only in presence of an excess of anhyd. Na_2CO_3 . The esters are prepared in C_5H_5N at 100°. R. S. C.

Structure of lumisterol. F. S. SPRING (J. Amer. Chem. Soc., 1938, 60, 3088—3089).—Misquotations of Weizmann *et al.* (A., 1938, II, 348) are corr. R. S. C.

Pyrovitamins- D_3 and their dehydro-derivatives. A. WINDAUS, M. DEPPE, and C. ROSEN-RUNGE (Annalen, 1938, 537, 1—10; cf. A., 1938, II, 58).—Vitamin- D_3 passes at 205° in vac. into non-cryst. pyrovitamin- D_3 (I) and non-cryst. isopyrovitamin- D_3 (II). (I) gives a cryst. 3:5-dinitro-



(I)



(II)

benzoate (III), m.p. 142°, $[\alpha]_D^{25} + 221^\circ$ in $CHCl_3$, a *p*-nitrobenzoate, m.p. 93°, $[\alpha]_D^{25} + 212^\circ$ in $CHCl_3$, and an acetate, (IV), m.p. 121°, $[\alpha]_D^{25} + 428^\circ$ in $CHCl_3$, whereas (II) affords a 3:5-dinitrobenzoate (V), m.p. 170°, $[\alpha]_D^{25} + 318^\circ$ in $CHCl_3$, a *p*-nitrobenzoate, m.p. 150°, $[\alpha]_D^{25} + 332^\circ$ in $CHCl_3$, and a non-cryst. acetate. Dehydrogenation of 7-dehydrocholesterol [$\Delta^5:7$ -cholestadien-3-ol] (VI) with $Hg(OAc)_2$ in $CHCl_3$ —AcOH at room temp. yields tetrahydrocholesterol [$\Delta^5:7:9:11$ -cholestatrien-3-ol] (VII), m.p. 112°, $[\alpha]_D^{25} + 146^\circ$ in $CHCl_3$; reaction proceeds somewhat more smoothly with its acetate and yields tetrahydro-

cholesteryl acetate (VIII), m.p. 88–89°, $[\alpha]_D^{20} +220^\circ$ in CHCl_3 , also obtained by acetylation of (VII). 7-Dehydrocholesteryl dinitrobenzoate is more slowly transformed into *tetrahydrocholesteryl dinitrobenzoate* (IX), m.p. 205°, $[\alpha]_D^{20} +166^\circ$ in CHCl_3 , also obtained from (VII) and $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{COCl}$ in $\text{C}_6\text{H}_5\text{N}$. (V) is slowly converted by $\text{Hg}(\text{OAc})_2$ in $\text{CHCl}_3\text{-AcOH}$ at room temp. into (IX), the identity of which is confirmed by hydrolysis and transformation into (VIII). (VI) and (II) differ therefore only in the steric arrangement of the substituents at C_{19} . Dehydrogenation of lumisterol-3 (and its derivatives) is relatively difficult since it is scarcely attacked at room temp. and does not give cryst. compounds when the temp. is raised. Its dinitrobenzoate is slowly converted into *dehydrolumisteryl-3 dinitrobenzoate* (X), m.p. 120°, $[\alpha]_D^{20} +16^\circ$ in CHCl_3 , also obtained by dehydrogenation of (III). (IV) is transformed by $\text{Hg}(\text{OAc})_2$ into *dehydrolumisteryl-3 (dehydropyrovitamin-D₃) acetate*, m.p. 103–104°, $[\alpha]_D^{20} +252^\circ$ in CHCl_3 , which has the same spectrum as dehydroergosterol. Lumisterol-3 and (I) differ therefore solely in the steric arrangement of the substituents at C_{19} . H. W.

Sterols. XLVII. Reduction products of œstrone. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1938, 60, 2927–2928).— α -œstradiol [obtained with β -œstradiol in good yield from œstrone by $\text{Al}(\text{OPr}^i)_3$ with $\text{H}_2\text{-PtO}_2$ and a little HCl in EtOH gives œstrane-3:17(α)-diol (I), m.p. 204° (A., 1938, II, 407), and a mol. compound (II), $\text{C}_{18}\text{H}_{30}\text{O}_2\cdot\text{C}_{18}\text{H}_{30}\text{O}$, m.p. 175°. With $\text{CrO}_3\text{-AcOH}$ at room temp. (I) and (II) give œstranediol, m.p. 170°. C_{17} of (I) has the α configuration since it is obtained also (Dierscherl, A., 1936, 472) by catalytic reduction of œstrone. R. S. C.

Derivatives of œstradiol.—See B., 1939, 104.

5-Bromo-2-methoxyphenylacetonitrile and its derivatives. M. PATY (Bull. Soc. chim., 1938, [v], 5, 1676–1685).—2:5:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}_2\cdot\text{CN}$ (I), b.p. 182.5–183°/13 mm., m.p. 65°, best (96% yield) obtained from the chloride and KCN in aq. EtOH , with $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (5:1) gives 5-bromo-2-methoxyphenylacetamide, m.p. 170°, or with 50% KOH gives the acid, which at 285° loses H_2O to yield the anhydride, m.p. 166.5°. With ROH-HCl (I) gives *Me*, b.p. 171–173°/18 mm., *Et*, b.p. 176–177.5°/18 mm., *Pr*, b.p. 185–186°/18 mm., and CH_2Ph 5-bromo-2-methoxyphenylacetate, m.p. 50°. The Na derivative of (I), prepared by NaNH_2 in Et_2O , with RHal gives α -5-bromo-2-methoxyphenyl-propio-, b.p. 174–176°/14 mm., -n-butyro- (II), b.p. 179–181°/14 mm., and -n-valero-nitrile, b.p. 186–187.5°/14 mm., whence α -5-bromo-2-methoxyphenyl- α -ethyl-n-butyronitrile, m.p. 58°, b.p. 189–191.5°/14 mm., and - α -methyl-n-valeronitrile, b.p. 191–193.5°/17 mm., are similarly, but more slowly, obtained. With $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (2:1) (II) gives α -5-bromo-2-methoxyphenylbutyramide, m.p. 101°, and with KOH in 95% EtOH gives this amide and the corresponding acid (75%), m.p. 98.5°. 2:5:1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHN}\cdot\text{CN}$ reacts with MeI (to give α -4-methoxy-m-tolylpropionitrile, b.p. 142–144°/15

mm.) as rapidly as does $\text{CHPhNa}\cdot\text{CN}$, and the slower reaction of (I) must be due to the nuclear Br.

R. S. C.

Preparation of substituted mandelic acids and their bacteriological effects. II. J. L. RIEB-SOMER, R. BALDWIN, J. BUCHANAN, and H. BURKETT (J. Amer. Chem. Soc., 1938, 60, 2974–2976).—*Et₂ hydroxy-p-n-propyl*-, b.p. 170–175°/4–5 mm. (40%), -p-n-butyl-, b.p. 176–177°/4–5 mm. (59%), -p-n-amyl-, b.p. 199–204°/4–5 mm. (51%), -p-tert-amyl-, b.p. 178–179°/4–5 mm. (95%), and -2:3:5:6-tetramethyl-phenylmalonate, b.p. 195–210°/27 mm., p-n-propyl-, m.p. 126–126.5° (20%), p-n-butyl-, m.p. 116.5–117° (25%), p-n-, m.p. 112.5° (8%), p-iso-, m.p. 87–87.5° (16%), and p-tert-amyl-, m.p. 73–74° (53%), pentamethyl-, m.p. 180–181° (9%), 2:3:5:6-tetramethyl-, m.p. 163° (1.3%), p-bromo-, m.p. 117.5° (8.8%), and p-iodo-, m.p. 135–136° (7.2% yield), mandelic acid are prepared (method: A., 1938, II, 278). Only the Br- and I-acids have greater effect on *B. coli in vitro* than has $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$. PhMe , $\text{CO}(\text{CO}_2\text{Et})_2$ (I), and SnCl_4 give a 1:1:1 additive compound. SnCl_4 and (I) give an unstable compound. R. S. C.

Acid amides as hypnotics. I. Acylcarbamides. II. Acetamides. F. F. BLICKE and A. P. CENTOLELLA (J. Amer. Chem. Soc., 1938, 60, 2923–2924, 2924–2926).—I. The following are prepared, but none of the carbamides has noteworthy hypnotic activity when injected peritoneally into white rats. β -Phenylethyl-propyl-, m.p. 123–124° (*Et₂* ester, b.p. 190–195°/14 mm.), -isopropyl-, m.p. 129–130° (*Et₂* ester, b.p. 204–206°/24 mm.), -isobutyl-, m.p. 136–137° (*Et₂* ester, b.p. 205–208°/20 mm.), -allyl-, m.p. 128–129° (*Et₂* ester, b.p. 205–208°/20 mm.), and - β -cyclohexylethyl-malonic acid, m.p. 134–135° (*Et₂* ester, b.p. 255–260°/30 mm.); ethyl- γ -phenylpropyl-, m.p. 148–149° (*Et₂* ester, b.p. 195–200°/18 mm.), - δ -phenylbutyl-, m.p. 114–115° (*Et₂* ester, b.p. 216–220°/22 mm.), - ϵ -phenylamyl-, m.p. 106–107° (*Et₂* ester, b.p. 230–235°/25 mm.), - ζ -phenylhexyl-, m.p. 67–68° (*Et₂* ester, b.p. 227–233°/18 mm.), and -cinnamyl-malonic acid, m.p. 133–134° (*Et₂* ester, b.p. 215–220°/30 mm.). α - β' -Phenylethyl-n-, b.p. 195–200°/20 mm. (chloride, b.p. 164–169°/19 mm.), and -iso-valeric, b.p. 198–204°/35 mm., - Δ^2 -pentenoic, b.p. 196–199°/22 mm. (chloride, b.p. 205–210°/15 mm.), and - γ -cyclohexyl-n-butyric acid, b.p. 245–250°/19 mm. (chloride, b.p. 220–225°/25 mm.); α - β' -phenylethyl- γ -methyl-n-valeric acid, b.p. 200–203°/20 mm. (chloride, b.p. 216–222°/18 mm.); α -ethyl- δ -phenyl-n-valeric, b.p. 193–196°/18 mm. (chloride, b.p. 217–220°/30 mm.), - ϵ -phenyl-n-hexzoic, b.p. 227–230°/50 mm. (chloride, b.p. 190–194°/22 mm.), - ζ -phenyl-n-heptoic, b.p. 213–219°/20 mm. (chloride, b.p. 199–204°/20 mm.), - η -phenyl-n-octoic, b.p. 218–222°/17 mm. (chloride, b.p. 206–210°/21 mm.), and - δ -phenyl- Δ^2 -n-pentenoic acid, b.p. 215–220°/35 mm. (chloride, b.p. 184–190°/20 mm.). α -Ethyl-n-butyryl-N-methylcarbamide, m.p. 93–95°; α -ethyl-n-valeryl-, m.p. 200–201°, -n-heptyl-, m.p. 138–139°, -n-octyl-, m.p. 126–127°, - γ -cyclohexyl-n-butyryl-, m.p. 176–177°, - β -phenylpropionyl-, m.p. 141–142°, - γ -phenyl-n-butyryl-, m.p. 152–153°,

-*δ*-phenyl-*n*-valeryl-, m.p. 143—145°, -*ε*-phenyl-*n*-hexoyl-, m.p. 137—138°, -*ζ*-phenyl-*n*-heptoyl-, m.p. 120—121°, -*η*-phenyl-*n*-octoyl-, m.p. 122—123°, and -*δ*-phenyl-*Δ*²-*n*-pentenoyl-, m.p. 139—140°, -carbamide; *α*-ethyl-*n*-hexoyl-*N*-methyl-, m.p. 77—78°, *α*-bromo-*α*-ethyl-*n*-hexoyl-, m.p. 84—85°, *α*-β'-cyclohexylethyl-*γ*-cyclohexyl-*n*-butyryl-, m.p. 175—176°, *γ*-phenyl-*n*-butyryl-, m.p. 174—175°, and *γ*-phenyl-*α*-β'-phenylethyl-*n*-butyryl-, m.p. 149—150°, -carbamide; *α*-β'-phenylethyl-*n*-, m.p. 148—150°, and -iso-valeryl-, m.p. 157—158°, -*Δ*²-*n*-pentenoyl-, m.p. 115—116°, -*n*-hexoyl-, m.p. 117—118°, and -*γ*-cyclohexyl-*n*-butyryl-, m.p. 148—149°, -carbamide; *γ*-methyl-*α*-β'-phenylethyl-*n*-valerylcarbamide, m.p. 149—150°.

II. The following are prepared, those marked * being strong hypnotics when injected as above. *α*-Ethyl-*n*-butyr-thioamide*, m.p. 80—81°, -*N*-ethylamide, m.p. 79—80°, and -butylamide, m.p. 34—35°; *α*-ethyl-*n*-hexo-amide*, m.p. 106—107° (lit., 101—102°), -methylamide*, m.p. 69—70°, -ethylamide, m.p. 58—59°, -β'-hydroxyethylamide, m.p. 47—49°, b.p. 199—200°/15 mm., and -butylamide, b.p. 177—178°/5 mm.; *α*-ethyl-*n*-heptamide*, m.p. 102—103° (lit., 96°), and -*n*-octoamide*, m.p. 106—107°; *γ*-cyclohexyl-*α*-ethyl-*n*-butyr-amide, m.p. 134—135°, -methylamide, m.p. 111—112°, -ethylamide, m.p. 96—97°, -β'-hydroxyethylamide*, m.p. 90—91°, and -butylamide, m.p. 61—62°; *γ*-cyclohexyl-*α*-β'-cyclohexylethyl-*n*-butyr-amide, m.p. 173—174°, -methylamide, m.p. 164—165°, and -ethylamide, m.p. 137—138°; *α*-β'-cyclohexylethyl-*n*-hexo-amide, m.p. 140—141°, -methylamide, m.p. 110—111°, -ethylamide, m.p. 94—95°, and -β''-hydroxyethylamide, m.p. 92—93°; *N*-*α*-ethyl-*n*-butyryl-, b.p. 159—160°/9 mm., and *N*-*α*-ethyl-*n*-hexoyl-morpholine, b.p. 185—186°/9 mm.; *NN'*-di-(*α*-ethyl-*n*-butyr)ethylenediamide, m.p. 230—231°; *α*-benzyl-*n*-butyramide, m.p. 117—118°; *α*-β'-phenylethyl-*n*-butyr-amide*, m.p. 105—106° (lit., 104°), -methylamide, m.p. 98—99°, and -ethylamide*, m.p. 72—73°; *γ*-phenyl-*α*-β'-phenylethyl-*n*-butyr-amide, m.p. 162—163°, -methylamide, m.p. 124—125°, and -butylamide, m.p. 86—87°; *γ*-cyclohexyl-*α*-β'-phenylethyl-*n*-butyramide, m.p. 170—171°; *α*-β'-phenylethyl-*n*-valer-amide*, m.p. 109—110°, -methylamide, m.p. 93—94°, -ethylamide*, m.p. 84—85°, -β''-hydroxyethylamide*, m.p. 74—75°, and -butylamide, m.p. 69—70°; *α*-β'-phenylethylisovaler-amide*, m.p. 121—122°, and -β''-hydroxyethylamide, m.p. 83—84°; *α*-β'-phenylethyl-*Δ*²-pentenoamide*, m.p. 90—91°; *α*-β'-phenylethyl-*n*-hexo-amide, m.p. 124—125°, -methylamide, m.p. 108—109°, -ethylamide, m.p. 71—72°, -β''-hydroxyethylamide, m.p. 66—67°, and -butylamide, m.p. 59—60°; *α*-β'-phenylethyl-*γ*-methyl-*n*-valeramide*, m.p. 89—90°; *α*-ethyl-*δ*-phenylvaler-, m.p. 118—119°, -*ε*-phenyl-*n*-hexo-, m.p. 107—108°, -*ζ*-phenyl-*n*-hepto-, m.p. 98—99°, -*η*-phenyl-*n*-octo-, m.p. 113—114°, and -*δ*-phenyl-*Δ*²-*n*-penteno-amide, m.p. 94—96°.

R. S. C.

Constituents of natural phenolic resins. XIII. Synthesis of *dl*-, *d*-, and *l*-hinokinin. R. D. HAWORTH and D. WOODCOCK (J.C.S., 1938, 1985—1989; cf. A., 1938, II, 323; Katsmatsu *et al.*, A., 1936, 1247; 1937, II, 21).—Piperonal and Et succinate in NaOEt-Et₂O at 0° for 7 days afford *α*-di-(3:4-methylenedioxybenzylidene)succinic acid, m.p. 207—

208° (+2AcOH), 228° ("anhyd.") (anhydride, m.p. 212—213°) (cf. Stobbe *et al.*, A., 1911, i, 373). The acid and Na-Hg in 1% NaOH at 80—90° (CO₂) give *meso*-*α*-di-(3:4-methylenedioxybenzyl)succinic acid (I), m.p. 240—241°, not resolvable by strychnine, brucine, or cinchonine. (I) and Ac₂O give *dl*(*trans*)-*α*-di-(3:4-methylenedioxybenzyl)succinic anhydride (II), m.p. 160—161°, hydrolysed by aq. NaOH to the *dl*-acid, m.p. 201° (decomp.). The latter is resolved by strychnine into the *l*-acid, m.p. 174—175°, [*α*]_D²⁰ -12.4° in COMe₂ [strychnine salt (+9.5H₂O), decomp. 260° (softens ~140°)], and the *d*-acid, m.p. 174—175°, [*α*]_D²⁰ +12.1° in COMe₂ [strychnine salt (+4H₂O), decomp. ~240° (softens at 140°)]. These with Ac₂O give the *l*(+)- (III), m.p. 143—144°, [*α*]_D²⁰ +21.5° in COMe₂, and *d*(-)- (IV), m.p. 143—144°, [*α*]_D²⁰ -21.4° in COMe₂, -anhydrides, respectively. (II) and Al-Hg in C₆H₆-Et₂O-H₂O afford *dl*(*trans*)-*α*-di-(3:4-methylenedioxybenzyl)butyrolactone, m.p. 108° [Br₂, m.p. 160°, and (NO₂)₂, m.p. 172°, derivatives]. (III) similarly affords *l*(*trans*)-*α*-di-(3:4-methylenedioxybenzyl)butyrolactone (V), m.p. 65—66°, [*α*]_D²⁰ -34° in CHCl₃ [Br₂, m.p. 136°, and (NO₂)₂-derivative, dimorphous, m.p. 163—164° and 184—185°], identical with *l*-hinokinin (=l-cubebinolide). (IV) similarly affords the *d*(*trans*)-isomeride of (V), m.p. 64—65°, [*α*]_D²⁰ +33.8° in CHCl₃ [Br₂, m.p. 136°, and (NO₂)₂-derivative, dimorphous, m.p. 161—162° and 183—184°]. Measurements of the rates of hydrolysis of the lactones and of lactonisation of the corresponding OH-acids confirm the identity of synthetic *l*-hinokinin; the natural lactone possesses probably the *trans*-configuration. A. T. P.

Action of erepsin and trypsin on tetrapeptides derived from two molecules of glycine, one molecule of *l*(+)-alanine, and one molecule of *l*(-)-tyrosine. E. ABDERHALDEN, R. ABDERHALDEN, H. WEIDLE, E. BAERTICH, and W. MORNEWEG (Fermentforsch., 1938, 16, 98—124; cf. Bergmann *et al.*, A., 1934, 809).—Carbobenzoyloxy-*l*-alanyl chloride (I) (free acid, new m.p. 91—92°) in Et₂O and glycyl-*l*-tyrosine [from chloroacetyl-*l*-tyrosine, m.p. 153° (Et ester, m.p. 86—87°), and NH₃] in cold approx. 0.5*N*-NaOH give 60% of carbobenzoyloxy-*l*-alanylglycyl-*l*-tyrosine, m.p. 128°, [*α*]_D²⁰ +6.9° in EtOH, converted by H₂+Pd-black in MeOH into *l*-alanylglycyl-*l*-tyrosine, also obtained in poor yield from *d*-*α*-bromopropionylglycyl-*l*-tyrosine, new m.p. 164°, and EtOH-NH₃. The tripeptide and carbobenzoyloxyglycyl chloride (II) similarly give the carbobenzoyloxy-derivative, [*α*]_D²⁰ +24.18° in EtOH, of glycyl-*l*-alanylglycyl-*l*-tyrosine, [*α*]_D²⁰ +18.44° in H₂O (cf. lit.). *O*-Acetyl-*N*-carbobenzoyloxy-*l*-tyrosyl chloride (III) and NH₂-CH₂-CO₂Et in CHCl₃ afford *O*-acetyl-*N*-carbobenzoyloxy-*l*-tyrosylglycine Et ester, m.p. 116°, hydrolysed (*N*-NaOH at room temp.) to *N*-carbobenzoyloxy-*l*-tyrosylglycine (+2H₂O), decomp. 111° (sinters at 90°), which is hydrogenated (Pd-BaSO₄, aq. MeOH) to *l*-tyrosylglycine, m.p. 266° (decomp.) (darkens 232° and sinters 262°), also prepared (cf. A., 1933, 1063) by hydrogenation of its dicarbobenzoyloxy-derivative. Dicarbobenzoyloxy-*l*-tyrosine has m.p. 97—99°. *l*-Tyrosylglycine and (II) afford carbobenzoyloxyglycyl-*l*-tyrosylglycine, m.p. 134°, [*α*]_D²⁰

+5.35° in EtOH, converted (H_2 +Pd) into *glycyl-l-tyrosylglycine*, $[\alpha]_D^{20} +24.12^\circ$ in H_2O , which with (I) gives *carbobenzyloxyalanyl-glycyl-l-tyrosylglycine* and thence *l-alanyl-glycyl-l-tyrosylglycine*, $[\alpha]_D^{20} -8.5^\circ$ in H_2O . *Carbobenzyloxy-l-alanyl-l-tyrosylglycine*, m.p. 146° [from *l-tyrosylglycine* and (I)], is converted (H_2 +Pd) into *l-alanyl-l-tyrosylglycine*, which with (II) affords the *carbobenzyloxy*-derivative, m.p. 99° of *glycyl-l-alanyl-l-tyrosylglycine*, $[\alpha]_D^{20} +21.6^\circ$ in H_2O . *Dicarbobenzyloxy-l-tyrosyl chloride* (IV) with *glycylglycine* yields *dicarbobenzyloxy-l-tyrosylglycylglycine*, m.p. 154—155°, whence *l-tyrosylglycylglycine*, decomp. 199° (darkens at 192°), $[\alpha]_D^{20} +42.8^\circ$ in 20% HCl, also obtained by hydrolysis ($N-NaOH$ -MeOH) of *O-acetyl-N-carbobenzyloxy-l-tyrosylglycylglycine Et ester*, m.p. 141° [from *glycylglycine Et ester* and (III)], to *N-carbobenzyloxy-l-tyrosylglycylglycine*, m.p. 215° (sinters 213°), and subsequent hydrogenation. *l-Alanyl-l-tyrosylglycylglycine*, $[\alpha]_D^{20} +35.58^\circ$ in H_2O , is obtained from its *carbobenzyloxy*-derivative, m.p. 113—114°, $[\alpha]_D^{20} +7.24^\circ$ in EtOH [prep. from (I) and the tripeptide]. *d- α -Bromopropionylglycylglycine*, m.p. 171°, $[\alpha]_D^{20} +30.22^\circ$ in 0.1N-NaOH, and 25% aq. NH_3 give *l-alanyl-glycylglycine* ($+H_2O$), m.p. 227° [*Et ester* (V) [*hydrochloride*, m.p. 129° (turbid), froths 154°, decomp. 211°]], which with (IV) affords *dicarbobenzyloxy-l-tyrosyl-l-alanyl-glycylglycine*, froths 127°, clear melt at 154°, decomp. 181° (*monocarbobenzyloxy*-derivative, froths 144°, decomp. 178°), whence *l-tyrosyl-l-alanyl-glycylglycine*, froths ~184°, decomp. 197°, $[\alpha]_D^{20} +23.39^\circ$ in dil. EtOH, also obtained (less pure) by hydrogenation of the reaction product from (III) and (V) in EtOAc. *Chloroacetyl-glycyl-l-tyrosine*, decomp. 184°, $[\alpha]_D^{20} +44.75^\circ$ in EtOH, with 25% aq. NH_3 at 37° gives *glycyl-l-tyrosine anhydride*, m.p. 296° (by loss of $CH_2Cl\cdot CO$), and *glycylglycyl-l-tyrosine*, m.p. 218—220° (decomp.); the last and *d-CHMeBr\cdot COCl* in 2N-NaOH afford *d- α -bromopropionyl*- and thence *l-alanyl-glycylglycyl-l-tyrosine*, decomp. ~194°, $[\alpha]_D^{20} +28.19^\circ$ in H_2O (corresponding *dl-alanyl* compound, decomp. 197°). *l-Tyrosyl-l-tyrosine*, m.p. >260°, $[\alpha]_D^{20} +32.5^\circ$ in H_2O , is prepared by Bergmann's method (*loc. cit.*) and by hydrolysis (approx. 0.5N-NaOH) of *l-tyrosine anhydride* (from *tyrosine Me ester*, m.p. 137°, at 140°).

The above tri- and tetra-peptides are hydrolysed by trypsin (carboxypolypeptidase) (from pig pancreas) or, better, by erepsin (aminopolypeptidase) (from pig's small intestine) or rabbit serum, but not by acylase. The changes in $[\alpha]_D^{20}$ confirm the view that aminopolypeptidase attacks the residue containing free NH_2 , and that carboxypolypeptidase attacks the residue containing CO_2H . The *N-carbobenzyloxy*-derivatives are generally hydrolysed by trypsin but not by erepsin or acylase (except for *N-carbobenzyloxy-l-tyrosyl-l-tyrosine* which undergoes 15% fission).

W. McC.
Syntheses in the carane group. III. Synthesis of carane. P. C. GUHA and D. K. SANKARAN (Ber., 1938, 71, [B], 2673—2675).—A fuller account of work already reported (A., 1938, II, 371). 4-Methyl- Δ^1 -cyclohexene-1-carboxylic acid gives an *anilide*, m.p. 106—107°, an *amide*, m.p. 148°, and a *p-toluidide*, m.p. 127—128°. The *anilide*, *amide*, and *p-toluidide* of trimethyldicyclo-[0:1:4]-heptanecarboxylic acid,

$CHMe\cdot CH_2\cdot CH-\frac{CH_2-CH_2-C(CO_2H)}{>CMe_2}$, have m.p. 98—99°, 124—125°, and 113—114°, respectively. H. W.

Re-esterification of phenolic esters of carboxylic acids in presence of inorganic salts. G. A. VARVOGLIS (Ber., 1938, 71, [B], 2488—2492).—Most of the experiments are performed with *p*- $C_6H_4(OBz)_2$ (I) but *o*- and *m*- $C_6H_4(OBz)_2$ and 2:1:4- $C_6H_3Cl(OBz)_2$ behave similarly. In the absence of catalysts little reaction occurs between (I) and isoamyl alcohol (II) the products being isoamyl benzoate, *p*- $OH\cdot C_6H_4\cdot OBz$ (III), and very little *p*- $C_6H_4(OH)_2$ (IV). $ZnCl_2$ and $AlCl_3$ are very effective giving exclusively (IV) and the alkyl benzoate (V). $ZnSO_4$, $CaCl_2$, and $MgCl_2$ are less active, the change proceeding only to (III) and (V); (IV) is formed in traces or not at all. $SnCl_2$ and Cu salts are still less efficient, the slight change which occurs resulting in (IV) and (V). $NaCl$ has no appreciable effect. Among alcohols [MeOH, EtOH, (II), $CH_2Ph\cdot OH$, $(CH_2\cdot OH)_2$] the best yields are obtained from those of relatively high b.p. Boiling MeOH and EtOH cause no appreciable change but at 130° under pressure the re-esterification is complete. Reaction, however, proceeds more slowly than with (II) under similar conditions. Extensive re-esterification takes place with $CH_2Ph\cdot OH$ and $(CH_2\cdot OH)_2$ in the absence of a catalyst if the experiment is sufficiently prolonged. In presence of catalysts ($ZnCl_2$) $CH_2Ph\cdot OH$ give intractable brown resins. H. W.

Transformation products of 2-chloro-4:5-dinitrobenzoic acid. H. GOLDSTEIN and W. GLAUSER (Helv. Chim. Acta, 1938, 21, 1513—1518; cf. A., 1938, II, 13).—Further examples of the mobility of NO_2 at C_{41} in 4:5:2-(NO_2) $_2C_6H_3Cl\cdot CO_2H$ (I) are cited. 33% NH_2Me converts (I) at 100° into 2-chloro-5-nitro-4-methylaminobenzoic acid, m.p. 280° (decomp.). 2-Chloro-5-nitro-4-dimethylamino-, m.p. 238—239° (decomp.), 4-ethylamino-, m.p. 242°, and 4-diethylamino-, m.p. 167°, benzoic acid are obtained similarly. (I) and $EtOH\cdot N_2H_4\cdot H_2O$ give the unstable 2-chloro-5-nitro-4-hydrazinobenzoic acid (N_2H_4 salt, m.p. 186—187°; Ac derivative, m.p. 265°), which with $COMe_2$ yields acetone-5-chloro-2-nitro-4-carboxyphenylhydrazone, m.p. 247°, and is converted by 2N- Na_2CO_3 at 100° into 6-chloro-3-hydroxybenzotriazole-5-carboxylic acid, decomp. 234.5°. (I) and $NHPh\cdot NH_2$ in boiling EtOH afford 2-chloro-5-nitro-4-phenylhydrazinobenzoic acid, m.p. 190—200° (very rapidly heated) or 246° after changing from red to yellow at 190—200°, transformed by glacial AcOH into 6-chloro-3-oxido-2-phenylbenzotriazole-5-carboxylic acid, m.p. 255.5°. (I) and Na_2S_2 in boiling EtOH yield 4:4'-dithiodi-2-chloro-5-nitrobenzoic acid, m.p. 316° (decomp.). 2-Chloro-4-iodo-5-nitrobenzoic acid, m.p. 210—211°, is obtained from 5:2:4- $NO_2\cdot C_6H_3Cl(NH_2)\cdot CO_2H$ by the diazo-method; boiling 2N-NaOH transforms it into 5:2:4- $NO_2\cdot C_6H_3Cl(OH)\cdot CO_2H$. It does not appear to be affected by conc. aq. NH_3 or by NH_2Ph in presence of anhyd. K_2CO_3 . With NH_2Ph -catalytic Cu it loses Cl and I . All m.p. are corr. H. W.

Schiff bases from 4-amino-*o*-tolunitrile. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1938, [v], 5, 1487—1489; cf. A., 1938, II, 491).—The

CHPh., m.p. 80°, *vanillylidene*, m.p. 132°, *piperonylidene*, m.p. 127°, and *o*-, m.p. 134° (sensitive to light), *m*-, m.p. 160°, and *p*-, m.p. 168° (best for identification) *-nitrobenzylidene* derivatives of 4:1:2-NH₂·C₆H₃Me·CN (*loc. cit.*) are described. A. T. P.

Rearrangement of *o*-carbamyl derivatives of diphenyl ether. B. T. TOZER and S. SMILES (J.C.S., 1938, 2052—2056; cf. A., 1939, II, 20).—Rearrangement of the amides is by NaOH (1.25 mols., 0.2N) in H₂O-COMe₂ (1:4) (unless stated otherwise), and is studied with regard to substituents in the phenoxy-nucleus and the character of the amide-N (theory discussed). 2-*p*-Nitrophenoxy-benzamide, m.p. 167° (50°; 1 hr.), *-benzanilide*, m.p. 127° (18°), and *-benz-m-nitroanilide*, m.p. 141° (18°) (also by piperidine or C₅H₅N at 18°), give *salicyl-4'-nitroanilide*, *-4'-nitrodiphenylamide*, m.p. 134°, and *-3':4'-dinitrodiphenylamide*, m.p. 168°, respectively. The last is hydrolysed to *o*-OH·C₆H₄·CO₂H and 3:4'-*dinitrodiphenylamine*, m.p. 217°, also synthesised from *m*-NO₂·C₆H₄·NH₂ and *p*-C₆H₄Br·NO₂ (method: Eckert *et al.*, A., 1915, i, 596). 1:2:4-C₆H₃Cl(NO₂)₂ and *o*-OH·C₆H₄·CO₂Me in MeOH-NaOMe at 18° (6 hr.) give *Me o-2':4'-dinitrophenoxybenzoate*, m.p. 88°. The corresponding acid, m.p. 164°, affords the *amide*, m.p. 121°, converted (18°) into *salicyl-2':4'-dinitroanilide*, m.p. 213°, also prepared by heating the *amide* at 200°, or synthesised from *salicylamide* and 1:2:4-C₆H₃Cl(NO₂)₂ in NaOEt-EtOH. 4-Nitrophenoxy-acetyl chloride and NH₂Ph give 4-*nitrophenoxyacetanilide*, m.p. 172°, which affords [in *N*-NaOH (1.25 mols.) at 100°, through (?) glycollo-4-nitrodiphenylamide (not isolable)], 4-nitrodiphenylamine. 4-*o*-Nitrophenoxytoluene-3-sulphonamide, m.p. 159°, and *-sulphonmethylamide*, m.p. 145° (the *-sulphonanilide* does not react), and *N*-NaOH (2.5 mols.) at 100° give 4-*hydroxytoluene-3-sulphon-o-nitroanilide*, m.p. 160°, and *-o-nitromethylanilide*, m.p. 135°, respectively; both anilides with Me₂SO₄ in alkali afford 4-*methoxytoluene-3-sulphon-o-nitromethylanilide*, m.p. 140°, also prepared by methylation of 4-*methoxytoluene-3-sulphon-o-nitroanilide*, m.p. 116°. 2:4-Bis-methylsulphonylphenyl *o*-nitrobenzoate, m.p. 186°, and SnCl₂-AcOH (saturated with HCl) at 16° afford 2:4-bismethylsulphonylphenyl anthranilate, m.p. 204°, not rearranged by alkali. 2:4:6:1-C₆H₂Cl₃·OH, *o*-NO₂·C₆H₄·SO₂Cl, and K₂CO₃ in boiling COMe₂, give 2:4:6-trichlorophenyl *o*-nitrobenzenesulphonate, m.p. 142°, converted by SnCl₂-AcOH into the *o*-aminobenzenesulphonate, m.p. 153°, unchanged or partly hydrolysed by boiling *N*-NaOH. 2:4:1-(MeSO₂)₂·C₆H₃·OH and *o*-NO₂·C₆H₄·SO₂Cl-K₂CO₃ give a product, reduced by SnCl₂-AcOH at 18° to 2:4-bismethylsulphonylphenyl *o*-aminobenzenesulphonate, m.p. 169°, unchanged by *N*-NaOH at 80°. *o*-Nitrobenzenesulphonacetamide, m.p. 190°, and SnCl₂-AcOH at 18°, or alkaline Na₂S₂O₄, give 3-methylbenz-1:2:4-thiadiazine 1:1-dioxide, m.p. 268°, also obtained by heating *o*-acetamidobenzenesulphonamide, m.p. 164°, (from the Na salt of the *o*-NH₂-compound and AcCl in C₆H₆) at 290°, or from *o*-NH₂·C₆H₄·SO₂NH₂ and Ac₂O-C₅H₅N at 18°. A. T. P.

Chlorination of *o*-thiolbenzoic acid. L. E. HART, E. W. MCCLELLAND, and (in part) F. S. FOWKES

(J.C.S., 1938, 2114—2117; cf. Price and Smiles, A., 1929, 62).—*o*-SH·C₆H₄·CO₂H or (*o*-CO₂H·C₆H₄·S)₂ and Cl₂ in CCl₄ give the *S*-dichloro-anhydride,

$$\left[\text{C}_6\text{H}_4 \begin{array}{c} \text{SO}_2 \\ \text{CO} \end{array} \right] \text{Cl} \text{ (I)}$$
 (mechanism discussed), which with PhSO₂·NH₂·C₅H₅N affords 2-*keto-1-benzene-sulphonyl-1:2-dihydrobenzothiazole S-oxide* (II), m.p. 182°, converted by H₂O₂-AcOH at 100° into *N*-benzenesulphonyl-*o*-benzoicsulphinide and PhSO₂·NH₂. (II) and 2N-NaOH give *o*-PhSO₂·NH·CO·C₆H₄·SO₂H, converted by boiling aq. HgCl₂ followed by HCl-EtOH into PhSO₂·NHBz. (I) with *p*-C₆H₄Me·SO₂·NH₂ and NH₂Ac, respectively, affords 2-*keto-1-p-toluene-sulphonyl*-, m.p. 179°, and *-1-acetyl*-, m.p. 150°, *-1:2-dihydrobenzothiazole S-oxide*. The latter substance, with H₂O₂-AcOH at 100°, gives *o*-benzoicsulphinide, with 2N-NaOH or HCl affords *o*-CO₂H·C₆H₄·SO₂H and 2:2'-dithiobenzoic acid, and with H₂O at 100° gives 2-*keto-1:2-dihydrobenzothiazole S-oxide*, m.p. 159°, converted by Zn-AcOH-HCl into *o*-thiolbenzamide, identified as disulphide. *o*-SH·C₆H₄·CO₂H and Cl₂ in anhyd. FeCl₃-CCl₄ give a product (A) which with H₂O yields *m*-chloro- and 3:5-dichloro-benzoic acid, and 5:5'-dichloro-2:2'-dithiobenzoic acid (III), m.p. 316—320° (decomp.) (mechanism of reaction discussed), but in boiling solution, 3:5:3':5'-tetrachloro-2:2'-dithiobenzoic acid, m.p. 263°, is formed. (III) and Zn-AcOH-HCl give 5-chloro-2-thiolbenzoic acid, m.p. 193° (cf. Krishna and Singh, A., 1928, 173), and (III) and CH₃Ac·CO₂Et-H₂SO₄ at 55° afford 5-chloro-3-hydroxy-1-thionaphthen. Dry NH₃ and (A) (not isolated) yield 4-chloro-2-*keto-1:2-dihydrobenzothiazole* (IV), m.p. 259—261°, and 5-chloro-2-aminothiolbenzoic acid, m.p. 199°; NH₂Ac-C₅H₅N afford (IV) and 4-chloro-2-*keto-1-acetyl-1:2-dihydrobenzothiazole*, m.p. 175—176° [also obtained from (IV) and Ac₂O]. The Ag salt of *o*-benzoicsulphinide (V), with PhSO₂Cl at 180° affords *N*-benzenesulphonyl-*o*-benzoicsulphinide, m.p. 202°, which with boiling 2N-NaOH gives *N*-benzenesulphonyl-*o*-sulphobenzamide, m.p. 209—212°. (V) and PhSO₂Cl or *p*-C₆H₄Me·SO₂Cl in C₅H₅N at room temp. give *O*-benzene-, m.p. 249°, and *O*-*p*-toluene-, m.p. 252°, *-sulphonyl-*o*-benzoicsulphinide*, respectively, converted by NaOH into (V). A. T. P.

7-Halogeno-1-naphthoic acids. H. GOLDSTEIN and H. A. FISCHER (Helv. Chim. Acta, 1938, 21, 1519—1523).—7:1-NH₂·C₁₀H₆·CO₂H (modified prep.) is converted (diazo-method) into 7-chloro-1-naphthoic acid, m.p. 243° (*Me* ester, m.p. 54°; *chloride*, m.p. 106°; *amide*, m.p. 237°; *anilide*, m.p. 185°), 7-bromo-1-naphthoic acid, m.p. 237° (*Me*, m.p. 55°, and *Et* ester, m.p. 46°; *chloride*, m.p. 106°; *amide*, m.p. 247°; *anilide*, m.p. 202°), and 7-iodo-1-naphthoic acid, m.p. 223° (*Me*, m.p. 88°, and *Et*, m.p. 64°, ester; *chloride*, m.p. 108°; *amide*, m.p. 248°; *anilide*, m.p. 217°). All m.p. are corr. H. W.

Hydrolysis of the amide and nitrile of 4-nitro-1-naphthoic acid. S. I. SERGIEVSKAJA and V. V. NESVADBA (J. Gen. Chem. Russ., 1938, 8, 934—936).—4:1-NO₂·C₁₀H₆·CO₂H is obtained by hydrolysis of its amide with conc. H₃PO₄ (5 hr. at 120—125°) or by the action of NaNO₂ in 50% H₂SO₄, or by hydrolysis of 4:1-NO₂·C₁₀H₆·CN with conc. HCl

(6 hr. at 134–140°) or H_2SO_4 – AcOH (18 hr. at 125–135°). R. T.

Anæsthetics of the naphthalene series. I. 4-Amino-1-naphthoic acid esters. S. I. SERGIEVSKAJA and V. V. NESVADRA (J. Gen. Chem. Russ., 1938, 8, 924–933).—4 : 1- $\text{NO}_2\text{-C}_{10}\text{H}_6\text{-CO}_2\text{Et}$ in EtOH is reduced (H_2 – Pt) to *Et* 4-amino-1-naphthoate, m.p. 81° (hydrochloride; *N-Ac* derivative, m.p. 183°). The Pr^α , b.p. 181–182°/4 mm., Pr^β , m.p. 71–72°, β -diethylaminoethyl, an oil (hydrochloride, m.p. 189–190°), γ -diethylamino- β -dimethylpropyl [hydrochloride, m.p. 153–155° (decomp.)], β -diethylaminoisopropyl [hydrochloride, m.p. 194–195° (decomp.)], and γ -diethylamino- α - β -dimethylpropyl ester (hydrochloride, m.p. 177–179°), and the chloride, m.p. 95–96°, of 4 : 1- $\text{NO}_2\text{-C}_{10}\text{H}_6\text{-CO}_2\text{H}$, and the Pr^α , m.p. 82–82.5°, Pr^β , m.p. 68.5–69.5°, β -diethylaminoethyl (hydrochloride, m.p. 212°; citrate, decomp. 114–116°), γ -diethylamino- β -dimethylpropyl [hydrochloride, m.p. 187–188° (decomp.)]; citrate, decomp. 146–147°], β -diethylaminoisopropyl (hydrochloride, m.p. 208°), and γ -diethylamino- α - β -dimethylpropyl ester [hydrochloride, m.p. 210–212° (decomp.)], of 4 : 1- $\text{NH}_2\text{-C}_{10}\text{H}_6\text{-CO}_2\text{H}$, are prepared similarly. The diethylaminoalkyl esters have pronounced local anæsthetic properties, being in many respects superior to cocaine and novocaine. R. T.

Kolbe-Schmidt synthesis. I. Mechanism of formation of 2 : 3-hydroxynaphthoic acid. N. F. SILIN and N. K. MOSCHTSCHNSKAJA (J. Gen. Chem. Russ., 1938, 8, 810–823).—The reaction $\beta\text{-C}_{10}\text{H}_7\text{-ONa}$ (I) + $\text{CO}_2 \rightarrow \text{C}_{10}\text{H}_7\text{-O-CO}_2\text{Na}$ (II) is reversed at higher temp. (140–160°). (II) rearranges to 2 : 1- $\text{ONa-C}_{10}\text{H}_6\text{-CO}_2\text{H}$ (III), which reacts at 145–160° as follows: (III) \rightarrow (I) + CO_2 ; (III) + (I) \rightarrow 2 : 1- $\text{ONa-C}_{10}\text{H}_6\text{-CO}_2\text{Na}$ (IV) + $\text{C}_{10}\text{H}_7\text{-OH}$; at 200–250° (IV) \rightarrow 2 : 3- $\text{ONa-C}_{10}\text{H}_6\text{-CO}_2\text{Na}$ (V). The max. possible yield of (V) is thus 50% on the (I) taken. The reactions leading to production of (IV) take place practically simultaneously at 150–160°, at which temp. the amount of CO_2 absorbed is half of that at 40–50°, and the same applies to direct production of (V) at 230°. Increasing the pressure to 45 atm. does not inhibit the reaction (III) \rightarrow (I) + CO_2 . The Na_2CO_3 content of the melt from which (V) is obtained is approx. \propto its content of tarry substances. R. T.

Determination of the fine structure of aromatic compounds. E. BERGMANN and T. BERLIN (J. Org. Chem., 1938, 3, 246–250).—2 : 3- $\text{OH-C}_{10}\text{H}_6\text{-COMe}$, new m.p. 121°, contains an ethylenic linking stabilised in position 2 : 3, since its oxime, m.p. 151°, gives an insol. *Cu* derivative; 2 : 3- $\text{OH-C}_{10}\text{H}_6\text{-CO}_2\text{H}$ is probably similarly constituted. 2 : 3- $\text{OH-C}_{10}\text{H}_6\text{-CO}_2\text{Me}$ with $\text{CH}_2\text{:CH-CH}_2\text{Br}$ or $\text{CHPh:CH-CH}_2\text{Br}$ and NaOH in COMe_2 , and distillation of the product in a vac., gives respectively *Me* 2-hydroxy-1-allyl-, m.p. 60° (acetate, b.p. 170°/0.3 mm.), and -1-cinnamyl-3-naphthoate, m.p. 132°, thus proving that the double linking in 2 : 3- $\text{CH}_2\text{:CH-CH}_2\text{-O-C}_{10}\text{H}_6\text{-CO}_2\text{Me}$ is in the 1 : 2 position. With basic *Cu* carbonate in quinoline 2-hydroxy-1-allyl-3-naphthoic acid, m.p. 203°; or 1 : 2-

$\text{CH}_2\text{:CH-CH}_2\text{-C}_{10}\text{H}_6\text{-OH}$ gives 2-methyl-4 : 5-1' : 2'-naphth-2 : 3-dihydrofuran, b.p. 125°/2 mm.

R. S. C.

3-Hydroxyfluorene-2-carboxylic acid and arylamides.—See B., 1939, 17.

Syntheses in the pinane group. V. Configuration of bromo- and hydroxy-pinic acids. P. C. GUHA and P. L. N. RAO (Ber., 1938, 71, [B], 2663–2665).—*dl*-Bromopinic acid (I), m.p. 154–155°, is converted by *Zn* dust and AcOH into the *trans*-pinic acid (II) (diamide, new m.p. 192°) from which it is derived and therefore has the *trans*-configuration. Since *dl*-hydroxypinic acid (III), m.p. 193–194°, is converted by PBr_3 into (I) it is a *trans*-compound. The change of configuration in the sequence (II) \rightarrow (I) \rightarrow (III) \rightarrow *cis*-norpinic acid must occur during the last stage. H. W.

Syntheses in the thujane group. VII. Complete synthesis of thujone. P. C. GUHA and M. S. MUTHANNA (Ber., 1938, 71, [B], 2671–2672).—Thujadicarboxylic [2-isopropylcyclopropane-1-carboxylic-2-acetic] acid (I) is converted by Ac_2O into its anhydride, which with MgMeI yields thujaketonic [1-acetyl-2-isopropylcyclopropane-2-acetic] acid. The still missing link in the complete synthesis of thujone is the conversion of umbellularic acid into (I). H. W.

Syntheses in the thujane group. VI. New synthesis of umbellularic acid. Attempted preparation of thujadicarboxylic and thujaketonic acid. P. C. GUHA and M. S. MUTHANNA (Ber., 1938, 71, [B], 2668–2671).—Partly an account of work previously abstracted (A., 1938, II, 364). The following appears new. *trans*-Umbellularic [1-isopropylcyclopropane-1 : 2-dicarboxylic acid] acid, m.p. 191–192°, is converted by the successive action of AcCl at 180° and boiling H_2O into the corresponding *cis*-acid (monohydrate, m.p. 94–95°). *Et* γ -methyl- Δ^6 -pentenoate and $\text{CHNa}(\text{CO}_2\text{Et})_2$ afford *Et* α -carbethoxy- β -isopropylglutarate, b.p. 135–140°/4 mm. [whence α -carboxy- β -isopropyl-, m.p. 160–162°, and β -isopropyl-glutaric acid (I), m.p. 101–102°], converted by Br in CCl_4 at 50° into *Et* α -bromo- α -carbethoxy- β -isopropylglutarate, b.p. 175–176°/3 mm. This when treated with NPhEt , quinoline, $\text{C}_5\text{H}_5\text{N}$, KOH , EtOH , or powdered KOH suspended in PhMe gives a debrominated compound which when treated with CH_2N_2 and hydrolysed yields (I) instead of the expected thujadicarboxylic acid. *Et* α -bromoisoxoate and $\text{CHNaAc-CO}_2\text{Et}$ appear to yield the solid *Et* 2 : 4-diketo-6-isopropylcyclohexane-1-carboxylate. H. W.

Strainless monocyclic rings. III. Synthesis of 2-methylcyclohexane-1-carboxylic-1-acetic acid and separation of its isomerides. M. QUDRAT-I-KHUDA, A. A. MALLICK, and (in part) A. MUKHERJI (J. Indian Chem. Soc., 1938, 15, 489–497; cf. A., 1938, II, 491).—2-Methylcyclohexanone, $\text{CN-CH}_2\text{-CO}_2\text{Et}$, and a little piperidine give *Et* 2-methylcyclohexylidenecyanoacetate, b.p. 165–167°/41 mm., converted by KCN into *Et* 1-cyano-2-methylcyclohexane-1-cyanoacetate, hydrolysed (50 hr.) to 2-methylcyclohexane-1-carboxylic-1-acetic acid, separated into isomerides, viz., A, m.p. 162° [anhydride (I),

b.p. 202°/24 mm.; *imide*, m.p. 107°; *anilic acid*, m.p. 150°; *p-toluidinic acid*, m.p. 179°; *p-tolylimide*, m.p. 140°; *p-naphthylamic acid*, m.p. 163°; β -*naphthylimide*, m.p. 169°] [hydrolysis of (I) with H₂O (8 hr.) gives an *isomeride B*, m.p. 155° (*anhydride*, b.p. 157°/12 mm.; *imide*, m.p. 110–111°; *anilic acid*, m.p. 143°)]; more sol. in C₆H₆ are the acids *C*, m.p. 153° (*Et₂* ester, b.p. 147–148°/18 mm.; *anhydride*, b.p. 142°/8 mm.; *imide*, m.p. 98°; *anilic acid*, m.p. 140°; *phenylimide*, m.p. 105°; *p-toluidinic acid*, m.p. 187°; *p-tolylimide*, m.p. 130°), and *D*, m.p. 142° (*anhydride*, b.p. 160–162°/8 mm.; *imide*, m.p. 105°), which affords the same anilic and *p*-toluidinic acid derivatives as does *C*. The anhydride of *C* is hydrolysed to *D*. The evidence supports the multiplanar configuration of the methylcyclohexane ring. A. T. P.

Lichen substances. XC. Orcinoldicarboxylic acid monomethyl ethers and the non-existence of the so-called isosquamatic acid. Y. ASAHINA, Z. SIMOSATO, and (in part) V. SAKURAI (Ber., 1938, 71, [B], 2561–2568; cf. A., 1933, 159, 504).—Me₂ orcinoldicarboxylate Me ether from thamnic and squamatic (I) acid has m.p. 125° and the m.p. of (I) is raised by suitable purification to 228°. There is therefore no difference between (I) and “isosquamatic” acid. Microchemical observation shows the complete absence of any depside from *Cladonia Boryi* (loc. cit.), in the examined specimens of which there must have been some *C. uncialis*. Successive treatments of Me *isovernate* with anhyd. HCN and HCl at –5° and with H₂O at 100° give *Me 5-hydroxy-6-aldehydo-3-methoxy-o-toluate*, m.p. 135° (*anil*, m.p. 138°), hydrolysed to the corresponding *acid*, m.p. 163–164°, which yields *evernaldehyde*, m.p. 64°, when dry-distilled. Me *p*-orsellinate Me₁ ether, HCl, AlCl₃, and HCN in Et₂O at 0° give exclusively Me 3-hydroxy-2-aldehydo-5-methoxy-*p*-toluate, m.p. 136°. Me *hæmatommate* (II), ClCO₂Et, and *n*-NaOH at 0° yield Me 2-O-*carbethoxyhæmatommate*, m.p. 96.5° (together with the 2:4-di-O-*carbethoxy*-derivative, m.p. 80°), converted by Ag₂CO₃ and MeI in COMe₂ into the corresponding *Me ether*, m.p. 144.5°, whence Me *hæmatommate 4-Me ether* (III), m.p. 87–88°, also obtained by partial demethylation of Me *hæmatommate Me₂ ether*. (II), CH₂PhCl, NaI, and K₂CO₃ in boiling COMe₂ afford, according to conditions, the corresponding (CH₂Ph)₂, m.p. 79°, or 2-CH₂Ph (IV), m.p. 112.5° (*p*-nitrophenylhydrazone, m.p. 278°), and 4-CH₂Ph ether (V), m.p. 91° (*p*-nitrophenylhydrazone, m.p. 249°; condensation product, m.p. 143.5°, with *o*-C₆H₄Me-NH₂). (IV) and (V) are converted by MeI and K₂CO₃ in boiling COMe₂ into *Me hæmatommate 2-CH₂Ph 4-Me ether* (VI), m.p. 65.5°, and 4-CH₂Ph 2-Me ether (VII), m.p. 80°, respectively. Debenzylation of (VI) gives (III) and of (VII) yields *Me hæmatommate 2-Me ether*, m.p. 64° (*anil*, m.p. 101°). Reduction (Pd–C in AcOH) of (VI) and (VII) leads to Me *rhizionate* and *isorhizionate* respectively. (VI) is oxidised (KMnO₄ in COMe₂) and then methylated to Me₂ orcinol-1:3-dicarboxylate 2-CH₂Ph 4-Me ether (VIII), m.p. 51°, whilst (VII) correspondingly gives 1-Me *H orcinol-1:3-dicarboxylate 4-CH₂Ph 2-Me ether*, m.p. 136°, converted by CH₂N₂ into the Me₂ ester (IX), m.p. 76°. Reduct-

ive debenzylation (Pd–C in AcOH) of (VIII) gives Me₂ orcinol-1:3-dicarboxylate 4-Me ether, m.p. 125°, identical with that derived from (I). (IX) similarly yields Me₂ orcinol-1:3-dicarboxylate 2-Me ether, m.p. 52.5°, hydrolysed to the corresponding dicarboxylic acid, m.p. 158° (decomp.) or (+H₂O) m.p. 158° after softening at about 100°, with a little unidentified material, m.p. 168°. H. W.

Action of organo-magnesium compounds on 1-bromocyclohexanealdehyde. B. TCHOUBAR and O. SACKUR (Compt. rend., 1938, 207, 1105–1106; cf. Bartlett and Rosenwald, A., 1934, 1221).—1-Bromocyclohexanealdehyde (I) with MgPhBr in Et₂O at 0° affords 1-phenylcyclohexanealdehyde (A., 1935, 1240). Similarly (I) with MgMeI and MgEtBr affords cyclohexyl Me and Et ketone, respectively. Reaction of (I) with MgRX involves migration of either H (R = alkyl) or R (R = aryl) in the intermediate C₅H₁₀>CBr·CHR·OMgX. J. L. D.

Nitrones. III. cis-trans-Isomerism of anils? F. KRÖHNKE (Ber., 1938, 71, [B], 2593–2595).—Repetition of the work of Sachs *et al.* (A., 1902, i, 377), Barrow and Griffith (J.C.S., 1921, 119, 212), and Bergmann and Hervey (A., 1929, 695) on the interaction of *p*-NO₂·C₆H₄·CH₂Cl and *p*-NO₂·C₆H₄·NMe₂ (I) shows that the assumed existence (A., 1929, 695) of *cis-trans* isomeric anils is erroneous. Aldehydes can be obtained from benzyl halides in manner other than through the nitrones. Thus CH₂PhCl, CH₂PhBr, or CH₂PhI and (I) in EtOH containing NaOH at 20° give much PhCHO, a little azoxydimethylaniline, but no nitrone. The same compounds are obtained from CH₂PhBr or CH₂PhI and (I) in EtOH without alkali; nitrone cannot be isolated although it is stable under these conditions. H. W.

Nitrones. II. F. KRÖHNKE (Ber., 1938, 71, [B], 2583–2593; cf. A., 1936, 1510).—Nitrone formation with 1 mol. of a NO-compound occurs if the group >CHHal, >CH·OH, or >CH·NC₅H₅·X is present and the methine-H is sufficiently activated by the other residues; pyridinium can be replaced by quinolinium or isoquinolinium. The important factor is the presence of the N:C double linking in a ring since this has a very activating effect on neighbouring CH₂ or CH groups in alkaline solution. CHPh:CH·CH₂Br and C₅H₅N in C₆H₆ at 20° followed by 2*N*·HClO₄ give *cinnamylpyridinium perchlorate*, m.p. 73–74°, transformed by *p*-NO₂·C₆H₄·NMe₂ (I) and NaOH in EtOH at 0–20° into *N-p-dimethylamino-phenylstyrylnitrone*, m.p. 180°. The following benzylpyridinium halides are obtained by heating the pyridine halide with about a 20% excess of C₅H₅N in EtOH at 100°. The nitrones are prepared from the pyridinium salt and the NO-compound in EtOH with the calc. amount of *n*-NaOH at 20–30°. The following new or revised data are given. phenyl-*N*-*p*'-dimethylaminophenyl nitrone, m.p. 144°, from benzylpyridinium bromide and (I); *p*-nitrobenzylpyridinium bromide, m.p. 219°, whence *p*-nitrophenyl-*N*-*p*'-dimethylaminophenyl nitrone, m.p. 206°; *p*-nitrobenzylidene-*p*'-dimethylaminoanil, m.p. 219–220°; *o*-nitrobenzylpyridinium chloride (+H₂O), m.p. 183–184° (corresponding *perchlorate*, m.p. 161–162°),

whence *o*-nitrophenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 134-5°; *m*-nitrobenzylpyridinium chloride, m.p. 191°, and *m*-nitrophenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 168-5°; *p*-chlorobenzylpyridinium bromide, m.p. 172-173°, and *p*-chlorophenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 178°; *p*-chlorobenzylidene-*p*'-dimethylaminoanil, m.p. 165-5°; *m*-chlorobenzylpyridinium chloride, m.p. 180°, and *m*-chlorophenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 118° (corresponding anil, m.p. 104°); *p*-bromobenzylpyridinium bromide, m.p. 150-151°, and *p*-bromophenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 193°; *p*-methoxybenzylpyridinium bromide, m.p. 164°, and *p*-anisyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 146-147°; *p*-methoxybenzylidene-*p*'-dimethylaminoanil, m.p. 145°; 1-naphthylmethylpyridinium bromide, m.p. 135° after softening at 114°, and 1-naphthyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 127-129° after softening; *S*-*p*-xylylenedipyridinium bromide (+2H₂O), m.p. 281-282° (corresponding perchlorate), and the dinitron, decomp. >225°, converted by *N*-NaOH into *p*-C₆H₄(CHO)₂ in 77% yield; *s*-*m*-xylylenedipyridinium bromide, m.p. 221° (perchlorate), and the dinitron, m.p. 193°, whence *m*-C₆H₄(CHO)₂ in 40% yield; *s*-*o*-xylylenedipyridinium bromide which undergoes side reactions with (I) and ultimately gives *o*-C₆H₄(CHO)₂ in only very modest yield; benzhydrylpyridinium bromide, m.p. 185° (corresponding perchlorate, m.p. 206-207°), and diphenyl-*N*-*p*'-dimethylaminophenylnitron, m.p. 135° (decomp.), which with 2*N*-HCl gives COPh₂ in 95% yield; phenylcarbethoxy-*N*-*p*'-dimethylaminophenylnitron, m.p. 133-5°. NPh₂CPH-CN, m.p. 72°, is obtained in 62% yield by the addition of PhNO in EtOH to CH₂Ph-CN and *N*-NaOH in EtOH.

H. W.

Preparation of aromatic aldehydes. B. HELFERICH, R. STREECK, and E. GÜNTHER (J. pr. Chem., 1938, [ii], 151, 251-256).—Gradual addition of 6:3:1-OH·C₆H₃(CH₂·OH)·CHO to HNO₃ (d 1.4) at >80° gives 4-hydroxyisophthalaldehyde, m.p. 108-109° (corr.) (bisphenylhydrazone), in 70% yield. Similarly *o*- and *p*-NO₂·C₆H₄·CH₂·OH give the corresponding aldehyde in 85% or 80% yield, respectively. *p*-C₆H₄(CHO)₂ is obtained in 80% yield from *p*-C₆H₄(CH₂·OH)₂. 4:6:1:3-C₆H₂Me₂(CH₂·OH)₂ affords 4:6-dimethylisophthalaldehyde, m.p. 107-108° [bisphenylhydrazone, m.p. 195° (decomp.)].

H. W.

Syntheses in the thujane group. VI. Synthesis of umbellulonic [2-acetyl-1-isopropylcyclopropane-1-carboxylic] acid. P. C. GUHA and M. S. MUTHANNA (Ber., 1938, 71, [B], 2665-2667).—An account of work previously reviewed (A., 1938, II, 336).

H. W.

Preparation of R-methyl ketones from keten. I. Preparation of acetophenone. B. N. DASCHKEVITSCH (J. Gen. Chem. Russ., 1938, 8, 779-782).—MgPhBr in Et₂O and keten at >30° yield a complex, which with H₂O at 50° gives COPhMe (30-35%).

R. T.

Condensation of paraformaldehyde with aromatic ketones. R. C. FUSON, W. E. ROSS, and C. H. MCKEEVER (J. Amer. Chem. Soc., 1938, 60, 2935-2936).—COPhMe, paraformaldehyde (I) (all pro-

portions), and a little K₂CO₃ in MeOH at room temp. (7 days) give β-benzoylpropane-αγ-diol CH₂ ether (II), b.p. 124-126°/3 mm., converted by conc. HCl at room temp. into CH₂O and αγ-dichloro-β-benzoylpropane, m.p. 56-57°, and thence by C₆H₆-AlCl₃ into COPh·CH(CH₂Ph)₂. H₂SO₄ hydrolyses (II) (CH₂O liberated), but the (OH)₂-ketone could not be isolated; an unstable, lachrymatory oil, b.p. 101-105°/3 mm., was obtained. COPhEt, (I), and K₂CO₃ in MeOH give β-benzoyl-*n*-propyl alcohol, b.p. 143-145°/5 mm. (phenylurethane, m.p. 86-87°), converted by cold H₂SO₄ into 2-methyl-α-hydrindone, b.p. 88-90°/3 mm. (2-Br-derivative, m.p. 72-73°), oxidised by HNO₃ to *o*-C₆H₄(CO₂H)₂.

R. S. C.

β-Benzoyl-αβ-diphenylpropionic [γ-keto-αβγ-triphenylbutyric] acid. (Miss) H. M. CRAWFORD (J. Amer. Chem. Soc., 1938, 60, 3078-3079).—COPh·CHPhNa (prep. by Na in Et₂O) and CHPhBr·CO₂Et give COPh·CHPh·CHPh·CO₂Et, hydrolysed by KOH-EtOH to γ-keto-αβγ-triphenylbutyric acid, m.p. 201-202° (Me, m.p. 147-148°, and Et ester, m.p. 147-5-148°), with a little of the form, m.p. 211-212° (Me, m.p. 158-5-159°, and Et ester, m.p. 138-139°) (Reimer *et al.*, A., 1908, i, 989). With 65% H₂SO₄ both acids give the lactone, m.p. 124-125°, of γ-hydroxy-αβγ-triphenyl-Δ^β-butenoic acid, from which they are both recovered by KOH-EtOH. CO-derivatives could not be obtained.

R. S. C.

Regulation of the catalytic reduction of unsaturated compounds and the ageing phenomena of platinum contacts. C. WEYGAND and A. WERNER (Ber., 1938, 71, [B], 2469-2474).—Hydrogenation (pure Pt-black from PtO₂) of CHPh·CH·CO·C₆H₄Me-*p* yields α-cyclohexyl-γ-*p*-methylcyclohexylpropane. Addition of a very small amount of FeCl₃ causes a somewhat more rapid but otherwise similar hydrogenation, whereas if a much larger proportion of FeCl₃ is used the reaction ceases after absorption of 2 H₂ with formation of CH₂Ph·CH₂·CH(OH)·C₆H₄Me. FeCl₂ and H₂O are necessary for the sp. restriction. The reaction is similar for several substances (CHPh·CHPh; diphenylbutadiene; CHPh·CH·COPh; *cis*- and *trans*-CHPh·CH·CO₂H); >CO is unchanged or is converted into >CH·OH whilst aromatic residues are unaffected. With the restricted catalyst it is readily possible to convert *trans*-(CHBz)₂ into (CH₂Bz)₂; this cannot be achieved otherwise even when the experiment is discontinued after absorption of 1 H₂. A difference in the absorptive capacity of *cis*- and *trans*-(CHBz)₂ is noted in the presence or absence of the restricting agent. With mg. quantities the experiments are readily reproducible but considerable variations are observed when higher concns. are used. It is suggested that the activity of Fe^{II} salts depends on the removal of the last traces of O from the catalyst by Fe^{III} ions. The activity of the catalyst diminishes with keeping.

H. W.

αβ-Unsaturated ketones obtained from acetophenone and their reaction with phenylhydrazine. L. C. RAIFORD and G. V. GUNDY (J. Org. Chem., 1938, 3, 265-272).—Br₁- and Cl₁-derivatives of vanillin

with $C_6H_4X \cdot COMe$ and NaOH give only monoacetophenone derivatives (cf. A., 1932, 515). *o*- $NO_2 \cdot C_6H_4 \cdot COMe$ does not react with 5-, nor *p*- $C_6H_4Cl \cdot COMe$ with 2-bromovanillin. The following are obtained: ω -2'-nitro-, m.p. 175–178°, and ω -5'-bromo-2'-nitro-vanillylideneacetophenone, m.p. 185–187° (decomp.); ω -5'-bromovanillylidene-*p*-methyl-, m.p. 146–147°, -*p*-methoxy- (also +AcOH), m.p. 138–140°, -*p*-hydroxy-, m.p. 229–230°, -*m*-nitro-, m.p. 270° (decomp.), -*p*-bromo-, m.p. 154–155°, -*o*-chloro-, m.p. 120–121°, and -*p*-chloro-, m.p. 164–167°, -acetophenone. 5-Nitrovanillin gives ω -5'-nitro-vanillylideneacetophenone, m.p. 139–140°, and α -diphenyl- γ -5-nitro-4-hydroxy-3-methoxyphenylpentane- α -dione, m.p. 150–151°, and 2:5-dichlorovanillin gives ω -2':5'-dichlorovanillylideneacetophenone, m.p. 139–141°, and α -diphenyl- γ -2:5-dichloro-4-hydroxy-3-methoxyphenylpentane- α -dione, m.p. 160–161°. With $NHPh \cdot NH_2$ or $p\text{-}NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$ under all conditions tried the products, $CHAr \cdot CH \cdot COAr$, give pyrazolines directly, as judged by failure to obtain NH_2Ph on reduction. The following are described. 1:3-Diphenyl- (I), m.p. 139–141°, 1-phenyl-3-*p*-bromophenyl- (II), m.p. 195–197°, 3-phenyl-1-*p*-nitrophenyl-, m.p. 211–213°, 3-*p*-chlorophenyl-1-*p*-nitrophenyl-, m.p. 214–215°, 1-*p*-nitrophenyl-3-*p*-tolyl-, m.p. 231–232°, and 1-*p*-nitrophenyl-3-*p*-hydroxyphenyl-, m.p. 255–256°, -5-5'-bromo-4'-hydroxy-3'-methoxyphenylpyrazoline; 3-phenyl-, m.p. 210–212°, and 3-*m*-nitrophenyl-, m.p. 237–238°, -1-*p*-nitrophenyl-5-6'-bromo-4'-hydroxy-3'-methoxyphenylpyrazoline; 3-phenyl-1-*p*-nitrophenyl-5-5'-bromo-2'-nitro-4'-hydroxy-3'-methoxyphenylpyrazoline, m.p. 220° (decomp.). With $Na \cdot EtOH$ 1:5-diphenyl-3-*p*-bromophenylpyrazoline gives 12% of 1:3:5-triphenylpyrazoline, and (II) gives 10% of (I), much starting material being recovered in both cases.

R. S. C.

Rearrangement in the benzoin series. F. L. JAMES [with R. E. LYONS] (J. Org. Chem., 1938, 3, 273–280).—Decomp. of benzoin to CH_2Ph_2 and CO_2 by H_3PO_4 at elevated temp. is largely prevented by catalysts. The best yield (53.9%) of $CHPh_2 \cdot CO_2H$ is obtained by the use of 60% H_3PO_4 and SiO_2 gel at 270°/24 hr. 4:4'-Dimethyl- and -isopropyl-benzoin give similarly only 25% of $(p\text{-}C_6H_4Me)_2CH \cdot CO_2H$ and <5% of $(p\text{-}C_6H_4Pr^i)_2CH \cdot CO_2H$, respectively, both without decomp., but $OH \cdot CPh_2 \cdot CPh$ is unchanged and *p*-methoxy-, *p*-dimethylamino-, *pp'*-dimethoxy-, and *o'*-chloro-*p*-methoxy-benzoin decompose. The reaction mechanism is discussed.

R. S. C.

Relative proportions of stereoisomeric oximes formed by oximation of unsymmetrical ketones. W. E. BACHMANN and (Miss) M. X. BARTON (J. Org. Chem., 1938, 3, 300–311).—In naming ketoximes the prefix *syn* or *anti* refers to the relative positions of the OH and the radical named first. $COPh \cdot C_6H_4Ph$, $NH_2OH \cdot HCl$, and C_5H_5N in abs. $EtOH$ give the *syn*- (I), m.p. 173°, and *anti*- (II), m.p. 200°, -oximes, a similar mixture being also obtained under Koller's conditions (A., 1892, 186). Conversion of the crude product, best by PCl_5 in thiophen-free C_6H_6 , into the amide, hydrolysis thereof, and separation of the acids shows the mixture to contain 49% of (I) and 51% of

(II). Under the conditions of oximation pure (I) or (II) is equilibrated to the same mixture. The same method of analysis shows the following yields of *syn*-oxime to be formed: $COPhR$, $R = p$ -48, *m*-50, and *o*-tolyl 23, *p*-anisyl 51, $p\text{-}C_6H_4Cl$ 44, and 2-fluorenyl 46; *o*-66, *m*-47, and *p*-tolyl $p\text{-}C_6H_4Ph$ ketone 34; α - or β - $C_{10}H_7$, or $p\text{-}C_6H_4Ph$ Me ketone 99%. Ph mesityl and 9-anthranyl ketones do not form oximes. 1-Acetylanthrane, m.p. 106.5–108° (lit., 103–105°), partly decomposes during oximation. Analogous results are discussed. The following are incidentally prepared. *p*-Phenylbenz-methyl-, m.p. 167°, -*o*-, m.p. 179.5–180°, -*m*-, m.p. 165–166°, and -*p*-tolyl-, m.p. 230–231°, -amide; *o*-, m.p. 256°, -*m*-, m.p. 270°, and *p*-tolu-*p'*-diphenylamide, m.p. 236–237°; 1-, m.p. 159–160°, and 2-naphthomethylamide, m.p. 108–109.5°; *m*-toluanilide, m.p. 125–125.5°; 2-benzamido-fluorene, m.p. 215°; fluorene-2-carboxyanilide, m.p. 255–256°.

R. S. C.

Local anaesthetics derived from benzoylbenzoic acids. B. SANDAHL and T. CHRISTIANSEN (Bull. Soc. chim., 1938, [v], 5, 1573–1580).— $o\text{-}C_6H_4Bz \cdot COCl$ (I) (prep. with $SOCl_2$) and $NEt_2 \cdot [CH_2]_2 \cdot OH$ in C_6H_6 at 100° (bath)/20 min. give β -diethylaminoethyl *o*-benzoylbenzoate [hydrochloride (II), m.p. 95–130°, which is probably mainly the lactone form]. One experiment, viz., (I) left in a desiccator for 3 weeks before use, and reaction for 2½ hr., gave the ketonic hydrochloride, m.p. 137–138°, also obtained in poor yield from (I) (prep. with PCl_5). The hydrochlorides of β -diethylaminoethyl *m*- and *p*-benzoylbenzoates have m.p. 143.5–144.5° and 138–139°, respectively. (II) only is a good anaesthetic, but is toxic.

A. T. P.

Partition principle as applied to the structures of enolic sodium derivatives of β -diketones and β -keto-esters. III. A. MICHAEL and N. WEINER (J. Org. Chem., 1938, 3, 372–384; cf. A., 1932, 254).— $COPh \cdot CH \cdot CPh \cdot ONa$ (prepared by $NaNH_2$ or $NaOMe$) with $ClCO_2Me$ (1 mol.) in dioxan at room temp. gives *Me dibenzoylacetate* (I), m.p. 116–117° (*Cu* derivative, m.p. 240°), some $CHBz \cdot CPh \cdot O \cdot CO_2Me$ (II), and, by further reaction [from (I)], $CO_2Me \cdot CBz \cdot CPh \cdot O \cdot CO_2Me$ (III) (not isolated pure), b.p. ~204–208° (slight decomp.)/2 mm.; 20–25% of CH_2Bz_2 is recovered. $MeOH \cdot NaOH$ converts (II) into (I) and CH_2Bz_2 . With 0.5 mol. of $ClCO_2Me$ in dioxan 25.1% of (I) and 17.2% of (II) are formed; in Et_2O , however, 7% of (I) and 13.8% of (II) are obtained, the difference being ascribed to a “solvent effect.” Sodiumbenzoylacetone with 0.5 mol. of $ClCO_2Me$ in Et_2O or dioxan gives mainly $CHBz \cdot CMe \cdot O \cdot CO_2Me$ with less *Me α -benzoylacetate* (IV), b.p. 136–137°/2 mm. (*Cu* derivative, m.p. 226–228°; obtained also from $CHAcNa \cdot CO_2Me$ and $BzCl$). If an excess of $ClCO_2Me$ is used, about equal amounts of γ -keto- α -carbomethoxyoxy- β -acetyl- α -phenyl- Δ^2 -butene, m.p. 87°, and *Me β -carbomethoxyoxy- α -benzoylcrotonate*, m.p. 97°, are formed (cf. A., 1931, 1035); these products are also obtained from $ClCO_2Me$ and the Na derivative of (IV), and their structure is proved by hydrogenation, followed by hydrolysis to $Ph \cdot [CH_2]_2 \cdot COMe$ and $COPhPr^i$, respectively. Thus, (IV) enolises in both possible ways.

The product, m.p. 166°, obtained from $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{CMe} : \text{CH} \cdot \text{CPh} : \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ by dil. AcOH (A., 1931, 1035) is the *semicarbazone*, $\text{CH}_2\text{Ac} \cdot \text{CPh} : \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$. R. S. C.

The "two forms" of symmetrical tetra-benzoylthane. H. KLEINFELLER and H. TROMMSDORFF (Ber., 1938, 71, [B], 2448—2450).—The product of the action of CHNaBz_2 on I (Abell, J.C.S., 1912, 101, 997) is $\alpha\alpha\beta\beta$ -tetrabenzoylthane (I), m.p. 212°, accompanied by $(\text{CBz}_2)_2$ (identified by its photochemical behaviour and conversion into $\text{C}_2\text{H}_2\text{AcBz}_3$). Hydrolysis of (I) gives $(\text{CH}_2\text{Bz})_2$. The "tetra-benzoylthane of lower m.p." obtained by Wesenberg (Diss., Leipzig, 1898) from CH_2Bz_2 , NaOEt , and I is identified as $\alpha\alpha\beta$ -tribenzoylthane, m.p. 155°, obtained also from CH_2BzI and CHNaBz_2 in COMe_2 . It is converted by Cl_2 in boiling AcOH into β -chloro- $\alpha\alpha\beta$ -tribenzoylthane, m.p. 90—91°, and by HCl in boiling AcOH into 3-benzoyl-2:5-diphenylfuran, m.p. 77—78° (oxime, m.p. 170—172°). H. W.

Stereochemistry of cyclanes. V. Stereoisomeric dibenzylidene derivatives. R. CORNUBERT, M. DE DEMO, R. JOLY, P. LOUIS, and A. STRÉBEL. VI. Stereoisomeric dibenzylidenecycloheptanones. Action of ultra-violet rays on diarylidenecyclanones. R. CORNUBERT, R. JOLY, and A. STRÉBEL (Bull. Soc. chim., 1938, [v], 5, 1490—1501, 1501—1505; cf. A., 1938, II, 235).—V. When 2:5-dibenzylidenecyclopentanone (I), m.p. 190°, is heated at near the b.p./15—20 mm. for 10—15 min., a stereoisomeride (II), m.p. 141°, is obtained (amongst other products). (I) and (II) are hydrogenated to the same 2:5-dibenzylcyclopentanone. (II) and Br give (method: Vorländer and Hobohm, A., 1896, i, 603) the tetrabromide of (I), together with a little of an (?) isomeride, m.p. 80—85°. cyclopentanone (III) and PhCHO with various condensing agents give (I) (best by NaOEt) and no (II) is isolated; with Na_2CO_3 or NMe_3 , some 2:5-di-(α -hydroxybenzyl)cyclopentanone, m.p. 178° [converted partly by heating in EtOH into an isomeride, m.p. 158°, also obtained from (III)— $\text{PhCHO} \cdot \text{NEt}_3$], is also formed. Dehydration of either diol gives only (I) (cf. A., 1930, 474). (III) and $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{CHO}$ in $\text{NaOEt} \cdot \text{EtOH}$ give the corresponding di- p -tolylidenecyclopentanone (IV), m.p. 235—236°; after heating at \sim b.p. for $\frac{1}{2}$ hr., distillation gives a stereoisomeride, m.p. 115°. A stereoisomeride is not obtained from dibenzylidenecyclohexanone (V), m.p. 118°, or by dehydration of the corresponding di- α -hydroxybenzyl derivatives, m.p. 160—163° and 153—156° (cf. Vorländer and Kunze, A., 1926, 1144). cycloOctanone and PhCHO (2 mols.) (as below) give a hydroxybenzylbenzylidene derivative, m.p. 134—135°, dehydrated (Ac_2O) to a liquid product, $\text{C}_{22}\text{H}_{22}\text{O}$ [? (CHPh) $_2$ derivative].

VI. cycloHeptanone and PhCHO in $\text{MeOH} \cdot \text{NaOMe}$ at 60—65° give the dibenzylidene derivative (VI), m.p. 108°, hydrogenated (Ni formate, EtOH , at 75°) to the dibenzyl compound (VII), b.p. 248—249°/20 mm. (oxime, m.p. 112°). (VI) at \sim b.p./18 mm. and distilled gives a stereoisomeric dibenzylidenecycloheptanone (VIII), m.p. 107°, also reduced to (VII). Irradiation (ultra-violet) experiments are recorded: (VI) (520 hr.) and (V) are unaltered, but (VIII) gives

some (VI); (II) is little affected but (I) and (IV) undergo some oxidation. The ketonic reactivity [with PhCHO to give tetrahydropyrones] of dibenzylcyclopentanone, -hexanone, and -heptanone (does not react) diminishes in the order quoted. A. T. P.

Synthesis of substances related to the steroids. XXV. K. H. LIN and R. ROBINSON (J.C.S., 1938, 2005—2008; cf. A., 1937, II, 196).— $\text{CMeNa}(\text{CO}_2\text{Et})_2$ and $\text{Ac}[\text{CH}_2]_2\text{Cl} \cdot \text{Et}_2\text{O}$ give *Et methyl- β -acetylthylmalonate*, b.p. 114—116°/0.4 mm., which when refluxed with $\text{NaOEt} \cdot \text{EtOH}$ affords 1-carbethoxy-1-methylcyclohexane-2:4-dione (I), m.p. 81.5—82.5°. $m\text{-OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CN}$ and anhyd. $\text{SnCl}_2 \cdot \text{Et}_2\text{O} \cdot \text{HCl}$ at 0° afford the aldimine stannichloride, decomp. (neutral PO_4''' buffer) to *m-methoxyphenylacetaldehyde*, b.p. 117—119°/13 mm. (semicarbazone, m.p. 130—131°); no CO-compound is isolated on condensation with (I). Dimethyldihydroresorcinol (dimedone) (II) and $\text{CH}_2\text{Ph} \cdot \text{CHO}$ in piperidine-EtOH give $\beta\beta$ -bis-(2':6'-diketo-4':4'-dimethylcyclohexyl)ethylbenzene, m.p. 164—165°, converted by boiling Ac_2O or $\text{P}_2\text{O}_5 \cdot \text{C}_6\text{H}_6$ into 9-benzyl-3:3:6:6-tetramethyloctahydroxanthene-1:8-dione, m.p. 125—126°. Piperonylacetaldehyde and (II) at 160—165° give a product containing some (?) 6:7-methylenedioxy-2-acetyl-1-methylnaphthalene [2:4-dinitrophenylhydrazones, m.p. 299—300° (decomp.)], probably formed from CH_2Ac_2 [by loss of CMe_2 from (II)]. γ -3:4-Dimethoxyphenylbutyryl chloride and *Et sodioacetylsuccinate* in Et_2O give a product, which with aq. $\text{KOH} \cdot \text{EtOH}$ affords mixed acids. Esterification (CH_2N_2) gives *Me dimethoxyphenylbutyrate* and *Me γ -keto- ζ -3':4'-dimethoxyphenylheptate*, b.p. 195—198°/0.3 mm. [free acid, m.p. 69—70° (semicarbazone, m.p. 158—159°)]. The lactone, b.p. 203—208°/0.22 mm., of γ -hydroxy- ζ -3':4'-dimethoxyphenylheptic acid is synthesised (method: loc. cit.). Air and HBr passed into eugenol *Me ether* in $\text{C}_6\text{H}_6 \cdot \text{BzO}_2\text{H}$ give a hydroxymethoxybromopropylbenzene, b.p. 160—163°/10 mm. Safrole and HBr with $\text{BzO}_2\text{H} \cdot \text{C}_6\text{H}_6$ or in presence of FeCl_3 or α -heptenylheptaldehyde give only β -bromodihydrosafrole. A. T. P.

Attempted synthesis of the antirachitic vitamin. III. K. DIMROTH and H. JONSSON (Ber., 1938, 71, [B], 2658—2662; cf. A., 1938, II, 326, 327).—cycloHexylidenecacetaldehyde condenses with *p*-methoxycyclohexanone to α -cyclohexylidene- β -2-keto-5-methoxycyclohexylidene-ethane, m.p. 84°, which is stable to air. Similarly cyclohexanone and 1-decahydronaphthylidenecacetaldehyde afford α -1-decahydronaphthylidene- β -2-ketocyclohexylidene-ethane, m.p. 82—83° [2:4-dinitrophenylhydrazones, m.p. 232—236° (decomp.)], or, under different conditions, 2:6-di-(1'-decahydronaphthylidene-ethylidene)cyclohexanone, m.p. 196°. The absorption spectra of the ketones are discussed. Reduction [$\text{Al}(\text{OPr}^t)_3$ in Pr^tOH] of α -cyclohexylidene- β -2-ketocyclohexylidene-ethane gives α -cyclohexylidene- β -2-hydroxycyclohexylidene-ethane, m.p. 124—125°. The following substances are incidentally described: 1-ethyldecahydro-1-naphthol, b.p. 124—126°/12.5 mm. (*p*-nitrobenzoate, m.p. 114°); 1-hydroxydecahydronaphthalene-1-acetic acid, m.p. 147° (from 1-ketodecahydronaphthalene, Zn , and $\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Et}$ in C_6H_6 , and subsequent hydrolysis),

converted by boiling Ac_2O into decahydronaphthylideneacetic acid, m.p. 185° , which is oxidised to *trans*-1-ketodecahydronaphthalene, m.p. 230° .

H. W.

(A) Tertiary amino-alcohols and enols from carvone. (B) Optically active zwitterions and enol-betaines. H. RUFF and H. GYSIN (Helv. Chim. Acta, 1938, 21, 1413—1432, 1433—1449; cf. A., 1931, 1300; 1934, 1224).—(A) Carvone oxido (improved prep.; cf. Treibs, A., 1932, 398, 1139) is converted by 30% NHMe_2 at $95\text{--}105^\circ$ into (mainly) 2-dimethylamino-3-hydroxy-2-methyl-5-isopropenyl-cyclohexanone (I), b.p. $70\text{--}72^\circ/0.008$ mm., $[\alpha]_D^{20} -55.16^\circ$, 3-dimethylamino-2-hydroxy-2-methyl-5-isopropenylcyclohexanone (II), b.p. $90^\circ/0.006$ mm., 156° (slight decomp.)/11 mm., $[\alpha]_D -40.85^\circ$, and a little 3-dimethylamino-2-methyl-5-isopropenyl- Δ^2 -cyclohexenone (III), b.p. $60\text{--}61^\circ/0.006$ mm., $[\alpha]_D +30.77^\circ$ (separated from one another partly by distillation under diminished pressure and partly through their perchlorates, with unchanged material and hydroxycarvone, m.p. 185° (semicarbazone, m.p. 222°). (I) gives a perchlorate, m.p. $173\text{--}174^\circ$, $[\alpha]_D^{20} -12.78^\circ$ in H_2O , semicarbazone, m.p. 164° , oxime, m.p. 136° , a somewhat unstable acetate, b.p. $144\text{--}146^\circ/10.5$ mm., and a methiodide, m.p. 163° . Partial hydrogenation (Ni in EtOH) of (I) yields 2-dimethylamino-3-hydroxy-2-methyl-5-isopropylcyclohexanone, b.p. $132\text{--}134^\circ/12.5$ mm., $[\alpha]_D^{20} -47.42^\circ$ in C_6H_6 (perchlorate, m.p. 156° ; semicarbazone, m.p. 134° ; methiodide, m.p. $180\text{--}181^\circ$), whereas complete hydrogenation gives the (?) diastereoisomeric 2-dimethylamino-2-methyl-5-isopropylcyclohexane-1:3-diols, (IV), b.p. $139\text{--}141^\circ/11$ mm., $[\alpha]_D^{20} -38.89^\circ$ in substance, -41.38° in C_6H_6 (methiodide, m.p. $175\text{--}176^\circ$; aurichloride, m.p. 124°), and (V), b.p. $149\text{--}151^\circ/11$ mm., $[\alpha]_D^{20} -37.13^\circ$ in C_6H_6 , which does not yield a methiodide or aurichloride. The relative position of the OH in (I) is established by the observation that (IV) absorbs 6 O when oxidised by $\text{Pb}(\text{OAc})_4$. (II) affords a perchlorate, m.p. $143\text{--}144^\circ$, $[\alpha]_D^{20} +9.86^\circ$ in H_2O , and a methiodide, m.p. $140\text{--}141^\circ$, but does not appear to yield an oxime or a semicarbazone. It is partly hydrogenated (Ni in 50% EtOH) to 3-dimethylamino-2-hydroxy-2-methyl-5-isopropylcyclohexanone, b.p. $157\text{--}159^\circ/13$ mm., $[\alpha]_D^{20} -39.16^\circ$ in C_6H_6 , which does not give cryst. derivatives, is not further hydrogenated by Pd-H_2 at $75^\circ/115$ atm. but yields a mobile Me ether, and is completely hydrogenated (Ni in EtOH at room temp. and then at 60°) to 6-dimethylamino-1-methyl-4-isopropylcyclohexane-1:2-diol (VI), b.p. $163\text{--}165^\circ/11$ mm., $[\alpha]_D^{20} -41.79^\circ$ in C_6H_6 (methiodide, m.p. 181° after softening at 179°); this absorbs 1 O when treated with $\text{Pb}(\text{OAc})_4$ but does not react with COMe_2 in presence of anhyd. ZnCl_2 . (III) forms a perchlorate, m.p. 164° , $[\alpha]_D^{20} -40.1^\circ$ in H_2O , and a methiodide, m.p. $154\text{--}155^\circ$ to a turbid melt. It does not give a semicarbazone. (I) is transformed by MgMeI into 2-dimethylamino-1:2-dimethyl-5-isopropenylcyclohexane-1:3-diol, b.p. $139\text{--}139.5^\circ/10.5$ mm., m.p. 42° , $[\alpha]_D^{20} -25.85^\circ$ in C_6H_6 (perchlorate, m.p. 163°). Similarly (II) affords 6-dimethylamino-1:2-dimethyl-4-isopropenylcyclohexane-1:2-diol, b.p. $158\text{--}159^\circ/11.5$ mm., $[\alpha]_D^{20} -2.92^\circ$ in C_6H_6 (perchlorate, m.p. $125\text{--}126^\circ$), and (III) yields 3-dimethylamino-1:2-dimethyl-5-isopro-

penyl- Δ^2 -cyclohexenol, b.p. $122\text{--}124^\circ/12.5$ mm., $[\alpha]_D^{20} -3.16^\circ$ in C_6H_6 , from which cryst. derivatives could not be prepared. Reduction of (I) with Na and boiling EtOH gives two bases, m.p. 166° and $103\text{--}104^\circ$. When heated at $140\text{--}145^\circ/12$ mm. with a little ZnCl_2 , (I) loses H_2O and passes into 6-dimethylamino-6-methyl-3-isopropenyl- $\Delta^{1:4}$ -cyclohexadienol (VII), b.p. $116\text{--}118^\circ/11$ mm., $[\alpha]_D^{20} -10.81^\circ$ [perchlorate, m.p. 141° ; acetate, b.p. $142.5\text{--}143.5^\circ/11$ mm.; Me ether (perchlorate, m.p. 131°) not obtainable by Purdie's method or with CH_2N_2 but with Me_2SO_4 and 30% NaOH; methiodide, m.p. 163°].

(B) (I) is converted by $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ into 6-hydroxy-2-keto-1-methyl-4-isopropenyl-1-cyclohexyldimethylcarbethoxymethylammonium bromide (VIII), which has m.p. 165° (partial decomp.) $[\alpha]_D +7.81^\circ$ in H_2O (mutarotation) if obtained in presence of H_2O and $[\alpha]_D -9.56^\circ$ in EtOH if prepared in the complete absence of H_2O . The aq. solution (0.01N.) of (VIII) is strongly acidic ($p_H \sim 3$) whereas in EtOH it is only weakly acidic. The perchlorate has m.p. 159° after softening at 152° . Addition of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ to the Ac derivative of (I) gives the corresponding ester hydrobromide, $\text{C}_{18}\text{H}_{30}\text{O}_5\text{NBr}$, m.p. $129\text{--}131^\circ$, $[\alpha]_D^{20} +13.81^\circ$ in EtOH, $+16.24^\circ$ in H_2O (no mutarotation); the corresponding non-cryst. betaine gives a perchlorate, m.p. 125° (decomp.) after softening at 115° , $[\alpha]_D^{20} -1.7^\circ$ in H_2O . The mutarotation of (VIII) is therefore ascribed to the production of the zwitterion

$$\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\left\langle\begin{array}{c}\text{CH}_2\cdot\text{CH}(\text{O}^-) \\ \text{CO}^+\end{array}\right\rangle\text{CMe}\cdot\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$$

(IX). Ag_2O transforms (VIII) into the neutral, amorphous betaine, $[\alpha]_D^{20} -12.0^\circ$ in H_2O , characterised as the perchlorate, $\text{C}_{14}\text{H}_{23}\text{O}_5\text{NCl}$, m.p. 162° after softening at 157° ; attempts to isolate (IX) by using Ag_2CO_3 or MgCO_3 in place of Ag_2O were unsuccessful. (II) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ slowly and incompletely give 2-hydroxy-3-keto-2-methyl-5-isopropenyl-1-cyclohexyldimethylcarbethoxymethylammonium bromide, m.p. 166° , $[\alpha]_D^{20} +5.86^\circ$ in H_2O , the aq. solution of which has $p_H \sim 6$; it is transformed by TIOH but not by Ag_2O into the corresponding betaine, $[\alpha]_D^{20} -11.8^\circ$ in H_2O , which is neutral in H_2O and does not give a well-defined perchlorate. (IV) unites rapidly with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ to 2:6-dihydroxy-1-methyl-4-isopropylcyclohexyldimethylcarbethoxymethylammonium bromide, m.p. $218\text{--}220^\circ$, $[\alpha]_D^{20} -10.3^\circ$ in H_2O (perchlorate, m.p. $196\text{--}199^\circ$), whereas the isomeric bromide from (V) has m.p. 201° , $[\alpha]_D^{20} +15.4^\circ$ in H_2O ; the corresponding, very hygroscopic betaine, $[\alpha]_D^{20} +7.5^\circ$ in H_2O , gives a perchlorate, m.p. 201° after softening at 194° . (VI) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ slowly give 2:3-dihydroxy-2-methyl-5-isopropyl-1-cyclohexyldimethylcarbethoxymethylammonium bromide, m.p. 187° , $[\alpha]_D^{20} -8.38^\circ$ in H_2O (perchlorate, m.p. 233°), which has $p_H \sim 5$ in H_2O ; the corresponding betaine, $\text{C}_{14}\text{H}_{27}\text{O}_4\text{N}$, m.p. $168\text{--}169^\circ$, $[\alpha]_D^{20} -29.3^\circ$ in H_2O (perchlorate, m.p. 245°), is described. (VII) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ give 2-hydroxy-1-methyl-4-isopropenyl- $\Delta^{2:5}$ -cyclohexadienyldimethylcarbethoxymethylammonium bromide, m.p. 129° , $[\alpha]_D \pm 0^\circ$ (perchlorate, m.p. $238\text{--}239^\circ$), which in H_2O has $p_H 3\text{--}4$; with TIOH it yields the true enol-betaine, m.p. $199\text{--}200^\circ$, $[\alpha]_D \pm 0^\circ$ (perchlorate, m.p. $242\text{--}243^\circ$), which has $p_H 6$ in H_2O . 3-Keto-2-methyl-5-isopropenyl- Δ^1 -cyclohexenyldimethylcarbethoxymethyl-

ammonium bromide, $[\alpha]_D^{20} -10.7^\circ$ in H_2O , is too hygroscopic to permit crystallisation and does not give a cryst. perchlorate. 6-Hydroxy-2-keto-1-methyl-4-isopropenyl-1-cyclohexyltrimethylammonium hydroxide, $[\alpha]_D^{20} -38.8^\circ$ in H_2O , has $p_H \sim 11$ in H_2O and gives an unstable perchlorate, m.p. 114° after softening at 108° . 2-Hydroxy-1-methyl-4-isopropenyl- $\Delta^{2,5}$ -cyclohexadienyltrimethylammonium hydroxide, m.p. 168° (perchlorate, m.p. $138-139^\circ$), is not a strong base, does not absorb CO_2 from the air, and is stable; it is also obtained from the enol base with Me_2SO_4 and NaOH. (I) and $CH_2Cl \cdot CH_2 \cdot OH$ at 100° give 6-hydroxy-2-keto-1-methyl-4-isopropenyl-1-cyclohexyldimethyl- β -hydroxyethylammonium chloride, m.p. 105° , which is neutral in H_2O ; the corresponding betaine base is amorphous and does not give cryst. salts. H. W.

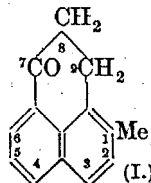
Properties of conjugated compounds. XX.
Diphenylketen as an addendum. E. H. FARMER and M. O. FAROOQ (J.C.S., 1938, 1925—1930).— $CPh_2 \cdot CO$ (I) and $\Delta^{1,3}$ -cyclohexadiene at room temp. form the anticipated 7-keto-8:8-diphenyl- Δ^2 -dicyclo-[4:2:0]-octene (II), m.p. $132-133^\circ$, the H_2 -derivative (III), m.p. 130° , of which is identical with the adduct obtained by prolonged heating of (I) and cyclohexene (cf. Staudinger and Suter, A., 1920, i, 556). (II) refluxed with KOH-MeOH for 70 min. gives (? trans)-2-benzhydryl- Δ^3 -tetrahydrobenzoic acid (IV), m.p. $148-149^\circ$, and the (?) cis-isomeride, m.p. 112° ; both forms with $KMnO_4$ in H_2O or $COMe_2$ afford $\epsilon\epsilon$ -diphenylpentane- $\alpha\gamma\delta$ -tricarboxylic acid (V), m.p. 210° (rapid heating, 228°); with the cis-form, a (?) stereoisomeride is also obtained. (III) refluxed with MeOH-NaOMe and a little H_2O affords 2-benzhydrylhexahydrobenzoic acid, m.p. $151-152^\circ$ [also by hydrogenation of (IV)], and an impure stereoisomeride, m.p. 123° . Oxidation ($KMnO_4$ - $COMe_2$) of (II) gives 2:2-diphenylcyclobutanone-3-carboxylic-4- β -propionic acid, m.p. $205-206^\circ$, converted by NaOH-MeOH into (V). Et α -bromoglutarate and $CHNa(CO_2Et)_2 \cdot C_6H_6$ (steam-bath) give Et butane- $\alpha\alpha\beta\delta$ -tetracarboxylate, b.p. $168-170^\circ/0.5$ mm., which with Na followed by $CHPh_2Br$ in C_6H_6 affords $(CHPh_2)_2$ and an ester, b.p. $252^\circ/1$ mm.; the latter and KOH-EtOH yield a cryst. product, m.p. $90-150^\circ$, which loses CO_2 with boiling dil. H_2SO_4 to yield (V) and a (?) stereoisomeride (cf. above). cyclopentadiene and (I) form the adduct, $CH \begin{smallmatrix} \diagup CH \\ \diagdown CH \end{smallmatrix} \begin{smallmatrix} \diagup CPh_2 \\ \diagdown CO \end{smallmatrix}$ (VI), m.p. $89-90^\circ$, hydrolysed with a very slight excess of KOH-MeOH to two isomeric forms, m.p. $148-149^\circ$, and $121-122^\circ$, of 2-benzhydryl- Δ^3 -cyclopentene-1-carboxylic acid, which with $KMnO_4$ - $COMe_2$ give isomerides, m.p. $186-187^\circ$ and $208-209^\circ$ (VII), respectively, of $\delta\delta$ -diphenylbutane- $\alpha\beta\gamma$ -tricarboxylic acid (cf. Simonsen et al., A., 1938, II, 20). (VI) and $KMnO_4$ - $COMe_2$ give an acid, hydrolysed by NaOH-MeOH to (VII). The polarised form of the ketens is discussed. A. T. P.

Experiments on the synthesis of substances related to the sterols. XXIV. Some derivatives of 2-keto-1:2:3:4-tetrahydronaphthalene. P. G. CROWLEY and R. ROBINSON (J.C.S., 1938, 2001—2005).—Et 3:4-dihydro- β -naphthoate, $N_2H_4 \cdot H_2O$ and EtOH, at 120° (bath) for 6 hr. give the hydrazide, m.p. 141° , converted through the azide into the

urethane, which when stirred with $0.33N \cdot H_2SO_4$ at 100° yields $NH_2 \cdot CO_2Et$ and 2-keto-1:2:3:4-tetrahydronaphthalene, b.p. $140^\circ/18$ mm. (phenylhydrazine, m.p. 108°). Et γ -m-anisylbutyrate, b.p. $170-171^\circ/20$ mm., isoamyl formate, and EtOH-free NaOEt in Et_2O at 0° —room temp. afford Et and isoamyl α -formyl- γ -m-anisylbutyrates, cyclised by H_2SO_4 - H_3PO_3 (d 1.75) at -10° , or by heating alone at $230-240^\circ/30$ mm., to mixed crude esters (A), b.p. $162-170^\circ/0.3$ mm., hydrolysed (20% NaOH) to 6-methoxy-3:4-dihydro- β -naphthoic acid, m.p. 176° (Et ester, b.p. $148^\circ/0.5$ mm.). $N_2H_4 \cdot H_2O$ -EtOH at 115° (bath) converts (A) into the corresponding hydrazide, m.p. 145° , converted through the azide into Et 6-methoxy-3:4-dihydro- β -naphthylcarbamate (I), m.p. 116° . (I) and $o\text{-}C_6H_4(CO)_2O$ at 220° yield phthal-6'-methoxy-3':4'-dihydro- β -naphthylimide, m.p. 195° . (I) and $0.6N \cdot H_2SO_4$ at 100° afford 2-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (II), m.p. 36° , b.p. $164^\circ/11$ mm. (2:4-dinitrophenylhydrazine, m.p. 132°), and $NH_2 \cdot CO_2Et$. (II) and $NaNH_2 \cdot Et_2O$ in N_2 , followed by $COMe \cdot [CH_2]_2 \cdot NEt_2 \cdot MeI$ (III) in EtOH, yield 2-keto-7-methoxy-2:3:4:9:10:12-hexahydrophenanthrene, b.p. $178-181^\circ/0.3$ mm. (2:4-dinitrophenylhydrazine, m.p. $186-187^\circ$), and a (?) dehydrogenated dimethoxy-tetrylidenetetralone, $C_{22}H_{18}O_3$, m.p. 247° . When excess of (III) is used, a substance, $(C_6H_8O)_n$, m.p. 228° (no ketonic properties), is also formed. Et γ -1-naphthylbutyrate (IV), b.p. $209-210^\circ/13$ mm. (cf. Fieser et al., A., 1935, 1495), and $HCO_2CH_2Bu^i$ -NaOEt- Et_2O afford a formyl derivative, which with H_2SO_4 - H_3PO_3 (d 1.75) at -5° for 3 hr., then hydrolysis (aq. NaOH), gives 3:4-dihydrophenanthrene-2-carboxylic acid, m.p. 234° (Et ester, b.p. $192-193^\circ/0.4$ mm.). The Et ester, b.p. $169^\circ/0.2$ mm. (cf. Cohen et al., A., 1936, 326), of γ -6-methoxy-1-naphthylbutyric acid (prep. by dehydrogenation of its 3:4- H_2 -derivative with S) similarly yields 7-methoxy-3:4-dihydrophenanthrene-2-carboxylic acid, m.p. 242° . Et γ -m-anisylbutyrate and KOEt- Et_2O -(CO_2Et) $_2$ give a product, converted by 96% H_2SO_4 at -15° (at -5° the anhydride is formed) into Et $_2$ 6-methoxy-3:4-dihydronaphthalene-1:2-dicarboxylate (V), b.p. $189-190^\circ/0.7$ mm. Hydrolysis with 20% aq. KOH gives acid + anhydride; boiling $CHCl_3$ then affords the anhydride, m.p. 166° , b.p. $193-195^\circ/0.6$ mm. (imide, m.p. 263°). (V) and H_2 -Pd- $SrCO_3$ in EtOH give, through the Et $_2$ ester, b.p. $192^\circ/0.66$ mm., 6-methoxy-1:2:3:4-tetrahydronaphthalene-1:2-dicarboxylic acid, m.p. 191° (methylimide, m.p. 126°).

A. T. P.

Derivatives of phenalene. W. KLYNE and R. ROBINSON (J.C.S., 1938, 1991—1994; cf. Koelsch et al., A., 1938, II, 19).—2:1- $C_{10}H_6Me \cdot CH_2Cl$ and $CHNa(CO_2Et)_2$ in dry C_6H_6 give Et 2-methyl-1-naphthylmethylmalonate, b.p. $190-195^\circ/2-3$ mm.; the acid, m.p. 172° (decomp.), loses CO_2 at $170-180^\circ$, to give β -2-methyl-1-naphthylpropionic acid, m.p. 93° , the chloride of which with $AlCl_3$ in light petroleum gives 1-methyldihydrophenalene-7-one (I), m.p. $54-55^\circ$ (yellow sample, m.p. $49-50^\circ$, is probably contaminated with methylphenalene) [2:4-dinitrophenylhydrazine, m.p. 250° (decomp.)] (cf. Cook and Hewett, A., 1934, 519). The oxime, m.p.



147—149°, of (I) in AcOH-EtOH at 55°, with 3% Na-Hg, gives 7-amino-1-methyldihydrophenalene [hydrochloride, m.p. 264—268° (decomp.) (sinters at 258°)]. (I) and $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}\cdot\text{EtOH}\cdot\text{KOH}$ afford methylperinaphthacridine, m.p. 134—137°. Reduction [$\text{Al}(\text{OPr}^i)_3\text{-Pr}^i\text{OH}$ at 110—115°] of (I) gives 7-hydroxy-1-methyldihydrophenalene, m.p. 126—127.5°, converted by the successive action of Na (in PhMe), CS_2 , and MeI into a hydrocarbon (picrate, m.p. 128—129.5°). A. T. P.

Syntheses in the hexahydrofluorene series. S. FUJISE (Ber., 1938, 71, [B], 2461—2468; cf. A., 1936, 1380).— o -Phenylhexahydrobenzoic acid (I), m.p. 105—106°, b.p. 120—123°/0.02—0.03 mm. (*l*-menthylamine salt, m.p. 118—122.5°, $[\alpha]_D^{17} -23.3^\circ$ in EtOH), obtained by reduction of $o\text{-C}_6\text{H}_4\cdot\text{Ph}\cdot\text{CO}_2\text{H}$ by Na and amyl alcohol, is not isomerised by HCl-AcOH at 130—135°. Catalytic reduction of $o\text{-C}_6\text{H}_4\cdot\text{Ph}\cdot\text{CO}_2\text{H}$ gives an *o*-cyclohexylbenzoic acid, m.p. 97.5—99.5°. (I) is converted (method: Cook and Hewett, A., 1936, 321) into 1:2:3:4:10:11-hexahydrofluorenone (II), m.p. 43.5—44°, b.p. 126—129°/0.8 mm., 98—103°/0.007 mm., which becomes pale yellow when kept or heated. When treated by different methods (II) gives an apparently non-homogeneous oxime (III), m.p. 101—108° or 106—116°; the product, m.p. 183—185°, of Cook and Hewett (*loc. cit.*) appears impure. Reduction of (III) catalytically (PtO_2 in AcOH), by Na-abs. EtOH, or by Na-Hg in abs. EtOH-AcOH affords a mixture of much β - (IV) and little α - (V) -hexahydrofluorenylamine (cf. Nakamura, A., 1930, 466); a similar mixture is obtained by the hydrogenation (PtO_2 in AcOH) of fluorenoneoxime. (IV) and (V) are separated through their acetates or benzoates (α , m.p. 146—147°; β , m.p. 183°). NaOAc and boiling Ac_2O convert (V) mainly into the α -N-Ac derivative, m.p. 148°, with a product, m.p. 215—218°, whilst (IV) gives a homogeneous Ac compound, new m.p. 258—259°. Benzoylation (Schotten-Baumann) of (IV) gives a homogeneous Bz derivative, m.p. 224—225°, also obtained from (V) with the α -Bz compound, new m.p. 168—170°. 2-Phenyl-4:5-dimethylhexahydrobenzoic acid affords 2:3-dimethylhexahydrofluorenone (VI), m.p. 68°, which becomes partly liquid on exposure to air. The oxime, m.p. 159—160°, obtained therefrom is essentially a single form; it is catalytically reduced to 2:3-dimethylhexahydrofluorenylamine (acetate, m.p. 172—173°; hydrochloride, m.p. 254—256°). Dehydrogenation (Se at 280° and then at 310°) of (VI) yields 2:3-dimethylfluorene and fluorenone. (II) behaves similarly. H. W.

Preparation of amines from partly hydrogenated phenanthrols. G. HABERLAND, G. KLEINERT, and H. J. STEGERT (Ber., 1938, 71, [B], 2623—2626).—3:4- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{CHN}_2$ and Ag_2O in boiling MeOH give 30% of 3-methoxy-2-naphthylacetic acid, b.p. 210°/1 mm., m.p. 183°. 3:2- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ in dry C_6H_6 is converted by the successive action of SOCl_2 and Et_2O sodioacetosuccinate followed by hydrolysis into β -3-hydroxy-2-naphthoylpropionic acid, m.p. 200° (Me ester, m.p. 104°), reduced (Clemmensen) to γ -3-hydroxy-2-naphthyl-n-butyric acid, m.p. 133°, which is cyclised by P_2O_5 in hot C_6H_6 to 10-hydroxy-

4-keto-1:2:3:4-tetrahydrophenanthrene (I), m.p. 226°. 3:7:2-(OH) $\cdot\text{C}_{10}\text{H}_5\cdot\text{CO}_2\text{H}$, is transformed by Ac_2O at 100° into 3:7-diacetoxy-2-naphthoic acid, m.p. 178°, converted by the successive action of SOCl_2 and CH_2N_2 in Et_2O into 3:7-diacetoxy-2-diazoacetone-naphthalene, m.p. 157°. 10-Hydroxy-4-keto-6-methoxy-1:2:3:4-tetrahydrophenanthrene (II), m.p. 218°, is best obtained by partial demethylation (boiling 48% HBr-AcOH) of the corresponding (OMe) $_2$ -compound. The OH of (I) is not advantageously replaced by NH_2 by Bucherer's method and 10-acetamido-4-keto-1:2:3:4-tetrahydrophenanthrene, m.p. 240°, is best obtained from (I), NaOAc, NH_4Cl , and AcOH at 210—215°; it is hydrolysed by 20% HCl at 100° to the NH_2 -ketone, m.p. 133° [2:4-dinitrophenylhydrazones, m.p. 230—235° (decomp.)]. (II) is converted into 10-acetamido-4-keto-6-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 175°.

H. W.

Experiments on the synthesis of substances related to the sterols. XXVI. R. ROBINSON and J. M. C. THOMPSON (J.C.S., 1938, 2009—2012; cf. A., 1938, II, 144).— $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I) and $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Br}$ in EtOH-NaOEt afford Et α -cyano- γ -phenylbutyrate, b.p. 182—183°/17 mm. (free acid, m.p. 74.5°), which with Me Δ^8 -dihydromuconate (II) in Et_2O -KOEt-EtOH gives an adduct (III), b.p. 220—225°/0.5 mm. (b.p. 225—230°/0.4 mm., from Et Δ^8 -dihydromuconate). (I) and (II) in NaOEt-EtOH afford a compound which with $\text{K}\cdot\text{PhMe}\cdot\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Br}$ gives (III), hydrolysed (20% aq. EtOH-KOH followed by conc. HCl) to 8-carboxy- γ -carboxymethyl- ζ -phenylheptonic acid, m.p. 139—140° [when purified through its Me ester (CH_2N_2), b.p. 200—205°/0.7 mm.], which with H_2SO_4 at 0° affords β -(1-keto-1:2:3:4-tetrahydro-2-naphthyl)adipic acid, m.p. 158—159°; the CO is inert. The chloride, b.p. 124—127°/0.5 mm., of Et H methronate and $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ give an ester, hydrolysed (method: Claisen, A., 1896, i, 557) to Et 4-carbomethoxy-5-methylfuran-2-acetoacetate, b.p. 153—156°/14 mm. Me γ -(6-methoxy-1-naphthyl)-butyrate (IV) and $\text{CO}_2\text{Me}\cdot[\text{CH}_2]_2\cdot\text{COCl}$ (V) in $\text{AlCl}_3\text{-PhNO}_2$ at <0°, then at room temp. for 36 hr., give a product which is methylated (*loc. cit.*) to γ -(6-methoxy-5-succinoyl-1-naphthyl)butyric acid (converted by boiling HI into 7-hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene) and γ -(6-methoxy-2- or 4-succinoyl-1-naphthyl)butyric acid, m.p. 201—202°. (IV) and PCl_5 afford the 5-Cl-ester, m.p. 76.5° [does not react with (V)], hydrolysed to γ -(5-chloro-6-methoxy-1-naphthyl)butyric acid, m.p. 189—190°, which with $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (3:1) at 100° for $\frac{1}{2}$ hr. yields 8-chloro-1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 219—220°. 1:2- $\text{C}_{10}\text{H}_6\cdot\text{Cl}\cdot\text{OMe}$, (V), and $\text{AlCl}_3\text{-PhNO}_2$, afford β -(5-chloro-6-methoxy-2-naphthoyl)propionic acid (VI), m.p. 199—200° (Me ester, m.p. 156°), converted by refluxing with HI (*d* 1.7)-AcOH and a little H_2O , for 18 hr., into β -(6-hydroxy-2-naphthoyl)propionic acid, m.p. 235° (decomp.), and by boiling dil. NaOCl-NaOH into approx. equal amounts of 5-chloro-6-methoxy-2-naphthoic acid (VII), m.p. 305° (boiling HI-AcOH gives 6:2- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$) and 2-naphthaldehyde (VIII), m.p. 141° [2:4-dinitrophenylhydrazones, m.p. 315° (decomp.)], oxidised by $\text{KMnO}_4\text{-NaOH}$ to (VII).

(VIII), $\text{CH}_2(\text{CO}_2\text{H})_2$, and $\text{C}_5\text{H}_5\text{N}$ + piperidine afford β -(5-chloro-6-methoxy-2-naphthyl)acrylic acid, m.p. 310°. Clemmensen reduction of (VI) gives γ -(5-chloro-6-methoxy-2-naphthyl)butyric acid, m.p. 137—138°, converted by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at 100° into 8-chloro-4-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 169—170°. A. T. P.

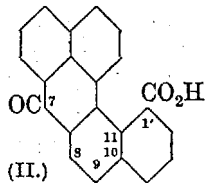
Synthesis of 4-keto-6 : 10-dimethoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene. G. HABERLAND and H. J. SIEGERT (Ber., 1938, 71, [B], 2619—2622; cf. A., 1938, ii, 144).—3 : 7 : 2-(OH) $_2$ C $_{10}$ H $_5$ CO $_2$ H is converted by Me_2SO_4 and NaOH into 3 : 7-dimethoxy-2-naphthoic acid, m.p. 140° (Me ester, m.p. 113°), the chloride (I), m.p. 88—90° (whence the amide, m.p. 218°), of which is transformed by CH_2N_2 in Et_2O into 3 : 7-dimethoxy-2-diazoacetophenanthrene, m.p. 115°; in hot AcOH this passes into 3-keto-6'-methoxynaphth-[2' : 3' : 4' : 5']-2 : 3-dihydrofuran, m.p. 172°. Et_2 sodioacetosuccinate and (I) in Et_2O give (after hydrolysis) β -3 : 7-dimethoxy-2-naphthylpropionic acid (II), m.p. 170° (Me ester, m.p. 107°), in very varying yield and Et_2 α -3 : 7-dimethoxy-2-naphthyl- α -acetylsuccinate, m.p. 120°. 3 : 7-Dimethoxy-2-naphthoic anhydride has m.p. 189°. 3 : 7-Dimethoxy-2-naphthyl Me ketone, m.p. 94°, and its 2 : 4-dinitrophenylhydrazones, m.p. 209°, are described. (II) is hydrogenated (Pd-C in Pr^6OH containing a little conc. HCl) to γ -3 : 7-dimethoxy-2-naphthyl-n-butyric acid, m.p. 157° (Me ester, m.p. 89°), cyclised by P_2O_5 in boiling C_6H_6 to 4-keto-6 : 10-dimethoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 89° (oxime, m.p. 162°; 2 : 4-dinitrophenylhydrazone, m.p. 102°). H. W.

Oxidative degradation of mesobenzanthrone and of its substitution derivatives. G. CHARRIER (Chim. e l'Ind., 1938, 20, 658—663).—A review, in which varying types of oxidation are discussed. The easier oxidation of the mesobenzanthrone system under alkaline conditions is ascribed to oxidation at $\text{C}_{(4)}$ and $\text{C}_{(6)}$, giving a phenanthrene system known to be sensitive to alkaline oxidation. E. W. W.

Sulphonation of mesobenzanthrone and some of its derivatives. R. R. PRITCHARD and J. L. SIMONSEN (J.C.S., 1938, 2047—2052; cf. Lauer and Irie, A., 1936, 1381).—Benzanthrone-7 (I) and 5% oleum at 145—150° (bath) or 18% oleum (Hg catalyst) at room temp., give (mainly) the 9-sulpho-derivative (II) [Na salt (+2H $_2$ O)] (cf. loc. cit.). A homogeneous chlorobenzanthrone-7 could not be obtained from the Na or K sulphonate and PCl_5 at 100° (bath). Crude (II) contains some 3-sulpho-derivative (III), as treatment with PCl_5 affords some 3-chlorobenzanthrone-7. It is improbable that (III) is the primary sulphonation product. The Na salt of (?) crude (II) with $\text{KClO}_3\text{-HCl}$ at 95° affords 3 : 9-dichloro- and (?) 9-chloro-benzanthrone; with NaOH-KOH at 220—230° followed by Me_2SO_4 + anhyd. Na_2CO_3 in $o\text{-C}_6\text{H}_4\text{Cl}_2$, 9 : 9'-dimethoxydibenzanthrone is obtained. Oxidation ($\text{CrO}_3\text{-AcOH-H}_2\text{O}$) of (II) affords 6-sulphoanthraquinone-1-carboxylic acid (IV), m.p. 271—274°, decomp. >275° [(NH $_4$) $_2$ salt (V)], purified through the Ba salt (+H $_2$ O). (V) and KClO_3 in aq. HCl at 95° give 6-chloroanthraquinone-1-carboxylic acid, m.p. 305—306° (Me ester, m.p. 190—191°). (V), freshly prepared MnO_2 , and aq. NH $_3$ at

200° give 6-aminoanthraquinone-1-carboxylic acid, m.p. 247—249° (sinters at 245°), and crude (?) 2-aminoanthraquinone, m.p. 295—297° (Ac derivative, m.p. 257—258°). (I) and 10% oleum at 165—170° give (?) benzanthrone-3 : 9-disulphonic acid; the Na salt and PCl_5 give a substance, m.p. 247—248°. 3-Chlorobenzanthrone and 5% oleum at 165—170° (bath) give the 9-SO $_3$ H derivative [Na salt, oxidised (CrO_3) to (IV)], but 10% oleum at 145—150° gives the 9 : ?-disulphonic acid (Na salt; impure dichloride, m.p. 230—255°). 9 : 10-Dichlorobenzanthrone (VI) and 5% oleum at 165—170° give the 3-SO $_3$ H derivative [Na salt (VII), with PCl_5 at 100° gives 3 : 9 : 10-trichlorobenzanthrone, m.p. 349—350°, also prepared from (VI) and $\text{Cl}_2\text{-AcOH}$ at 100°]. (VI) and $\text{CrO}_3\text{-AcOH}$ give 6 : 7-dichloroanthraquinone-1-carboxylic acid, m.p. 275—276° (Me ester, m.p. 197—198°), similarly obtained from (VII). 3-Bromobenzanthrone (VIII) and 5% oleum at 125—130° give the 9-SO $_3$ H derivative; the Na salt [oxidised (CrO_3) to (IV)] and PBr_5 at 100° (bath) yield the sulphonyl bromide, which in xylene at 155—160° gives 3 : 9-dibromobenzanthrone (IX), m.p. 255—256°, also obtained from (VIII) and $\text{Br-H}_2\text{O}$ at 40—100°. (IX) and $\text{CrO}_3\text{-aq. AcOH}$ afford 6-bromoanthraquinone-1-carboxylic acid, m.p. 298—299° (Me ester, m.p. 198—199°). 3-Nitrobenzanthrone and 5% oleum at 125—130° give the 9-sulphonic acid [the Na salt and $\text{CrO}_3\text{-AcOH}$ give (IV)]. A. T. P.

Anthanthrone and derivatives. V. Oxidation of 1'-carboxy-10 : 11-benzbenzanthrone-7. A. CORBELLINI and F. STEFFENONI. VI. Alkali fusion of anthanthrone. A. CORBELLINI and D. CRESPI (R. Ist. lombardo Sci. Lett. Rend., 1936, [ii], 69, 429—438, 580—586; Chem. Zentr., 1937, i, 1420—1421).—V. 1 : 1'-Dinaphthyl-8 : 8'-dicarboxylic acid (I) is converted by Ac_2O at 150—160° (bath) into 1'-carboxy-10 : 11-benzbenzanthrone-7 (II), m.p. 280—281° [Me ester (III), m.p. 155.5—156.5°, also obtained from the Me $_2$ ester of (I) and conc. H_2SO_4], together with a little anthanthrone (IV).

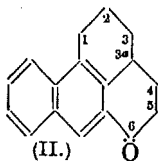


Hot dil. NaOH-Na $_2$ S $_2$ O $_4$ converts (III) into dihydroanthanthrone, oxidised (air) to (IV). Distillation of the Ba salt of (II) with Ba(OH) $_2$ in N $_2$ gives small amounts of unidentified products, m.p. 170° and 230°, whilst the Ba salt of (I) similarly affords perylene and 1 : 1'-dinaphthyl. Distillation of the NH $_4$ and Ag salts of (II) yields mainly (IV), also obtained by fusion of (II) with alkali. Oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7$, dil. H_2SO_4) of (II) gives some hydroxyanthanthrone (V), m.p. 304° (benzoate, m.p. 299°; Me ether, m.p. 299—300°), which when distilled with Zn dust affords anthanthrene.

VI. Fusion of (IV) with KOH-H $_2$ O, KClO_3 , and CuCl_2 at 150—250° gives a dihydroxyanthanthrone, decomp. >360° (dibenzoate, m.p. >350°; Me $_2$ ether, m.p. >350°), which is not obtained from (V) and is reduced (Zn dust) to anthanthrene. A similar compound is also obtained in the absence of oxidising agents. Molten alkali first reduces (IV) to dihydroanthanthrone [dibenzoate, m.p. 321—324° (blackens ~310°)]. H. B.

Enolic ethers of ketocyclopentanopolyhydrophenanthrene compounds.—See B., 1939, 104.

Estrogenic substances. Synthesis of keto-1:2-cyclopentenophenanthrenes. J. HOCH (Compt. rend., 1938, 207, 921–923; cf. Bachmann and Klotzel, A., 1938, II, 17).—1:2-cyclopentenophenanthrene with CrO_3 in cold AcOH affords ~50% of 1'-keto-1:2-cyclopentenophenanthrene (cf. *loc. cit.*). 1-Keto-1:2:3:4-tetrahydrophenanthrene, $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and $\text{Zn}\cdot\text{Hg}$ in C_6H_6 afford *Et* (3:4-dihydro-1-phenanthryl)acetate, b.p. 215–220°/2 mm., reduced ($\text{Na}\cdot\text{EtOH}$) to β -(1:2:3:4-tetrahydro-1-phenanthryl)ethyl alcohol, b.p. 225–230°/15 mm., which with PBr_3 gives a bromide (I) which after condensation with $\text{CH}_2(\text{CO}_2\text{Et})_2$, hydrolysis, and fusion gives γ -(1:2:3:4-tetrahydro-1-phenanthryl)butyric acid, m.p. 94–95°, dehydrogenated (S at 230°) to γ -1-phenanthrylbutyric acid, m.p. 152°. This is cyclised by SnCl_4 at 110° to 3-keto-3:4:5:6-tetrahydrochrysene, m.p. 222° (phenylhydrazone, m.p. 244–246°). (I) with KCN affords a nitrile, hydrolysed ($\text{EtOH}\cdot\text{KOH}$) to β -(1:2:3:4-tetrahydro-1-phenanthryl)propionic acid, m.p. 115°, cyclised with SnCl_4 to 1:2:3:3a:4:5-hexahydrobenzanthrone-6 (II), m.p. 115°.



Ketone from vitamin- D_2 . A. WINDAUS and K. BUCHHOLZ (Z. physiol. Chem., 1938, 256, 273–276).—Vitamin- D_2 (I) boiled for 12 hr. with COMe_2 , C_6H_6 , and $\text{Al}(\text{OBU}^t)_3$ gives a non-cryst. ketone (II) (alternative structures suggested) [semicarbazone (III), $\text{C}_{29}\text{H}_{45}\text{ON}_3$, m.p. 218–222° (decomp.); absorption max. at 293 μ .] which has an absorption max. at 265 μ . and an antirachitic action on rats ~300-fold inferior to that of (I). (II) is obtained from (III) by treatment with PhCHO ; decomp. with boiling $\text{AcOH}\cdot\text{H}_2\text{C}_2\text{O}_4$ gives, however, an isomeride [semicarbazone, m.p. 225–227° (decomp.); absorption max. at ~340 and 425 μ .] of (II). Reduction [$\text{Al}(\text{OPr}^i)_3$ in Pr^iOH] of (II) gives a poor yield of (I). W. McC.

Experiments on the synthesis of substances related to the sterols. XXIII. Formation of oestrone from a dicarboxylic acid obtained by degradation of oestrone methyl ether. F. LITVAN and R. ROBINSON (J.C.S., 1938, 1997–2001; cf. A., 1938, II, 144).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COCl}$ and KOH -free CH_2N_2 in Et_2O at -10° give a diazoketone, which in dioxan with $\text{Ag}_2\text{O}\cdot\text{aq. Na}_2\text{S}_2\text{O}_3$ at 70° (Arndt-Eistert reaction; cf. A., 1936, 844) affords γ -phenylbutyric acid, m.p. 49–50°. *d*-Homocamphoric acid (I) and $\text{H}_2\text{SO}_4\cdot\text{EtOH}$ afford the Et_2 ester, b.p. 128–130°/1 mm., converted by KOH into *Et H d*-homocamphorate (II), m.p. 78°, b.p. 145–147°/0.44 mm. (cf. Haller, A., 1889, i, 1205), better prepared from (I)- $\text{C}_6\text{H}_6\cdot\text{H}_2\text{SO}_4\cdot\text{EtOH}$ (limited amount) [the product obtained has m.p. 58.5–59.5°, $[\alpha]_D^{25} +57.5^\circ$ in EtOH , and submitted to the Arndt-Eistert reaction gives, after hydrolysis, (I)]. The chloride of (II) submitted to the Arndt-Eistert reaction gives a product hydrolysed by excess of HBr (*d* 1.5) to hydrocamphorylacetic acid, m.p. 137°, converted (Blanc's Ac_2O method) into homocamphor, m.p. 189.5–190.5° (2:4-dinitro-

E (A., II.)

phenylhydrazone, m.p. 232°). *O*-Methylcestrone with isoamyl nitrite in $\text{Bu}^t\text{OH}\cdot\text{KOBU}^t$ and N_2 gives 16-oximino-*O*-methylcestrone, m.p. 161–162° (decomp.), converted by $\text{PCl}_5\cdot\text{AcCl}$ at room temp. into a product, hydrolysed ($\text{EtOH}\cdot\text{KOH}$ for 14 days with subsequent addition of Zn dust) to *O*-methylcetric acid (III), m.p. 189–190° (mechanism discussed). Oximino-camphor and PCl_5 in AcCl give mainly the α -mononitrile of camphoric acid, m.p. 151–152°, but with isoamyl ether as solvent, the main product is the α -monoamide, m.p. 174–175°. (III) and $\text{CH}_2\text{N}_2\cdot\text{Et}_2\text{O}$ give the Me_2 ester, hydrolysed (aq. $\text{KOH}\cdot\text{MeOH}$) to the α -Me H ester, which is converted (Arndt-Eistert reaction) into *O*-methylhomo-cetric acid (IV) (Me_2 ester, m.p. 85°). The work of Bardhan (A., 1937, II, 63) is fully confirmed. Hydroxymethylene-*O*-methylcestrone gives Bardhan's acid, i.e., (IV), and an (?) isooxazole derivative. (IV) and PbCO_3 heated in a rotated tube give *O*-methylcestrone, demethylated [HI (*d* 1.9)- AcOH] to cestrone. A. T. P.

Two derivatives of cestrone. F. BERGEL and A. R. TODD (Biochem. J., 1938, 32, 2145–2146).—Cestrone β -naphthoate, m.p. 262–264°, produces prolonged oestrus in rats, although the onset is delayed longer than with cestrone. Cestrone diethylaminoethyl ether, m.p. 76–77° (hydrochloride, m.p. 190–191°), yields H_2O -sol. salts but has no oestrogenic activity. H. G. R.

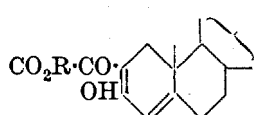
Hydroxyketo-cestrin, m.p. 258–260°, and its benzoate, m.p. 205–207°.—See B., 1939, 104.

Experiments on the synthesis of substances related to the sterols. XXII. Synthesis of α -norequilenin methyl ether. A. KOEBNER and R. ROBINSON (J.C.S., 1938, 1994–1997; cf. A., 1938, II, 496).—3- β -Naphthyl- Δ^2 -cyclopentenone-2-acetic acid and its *Me* ester, m.p. 100°, with H_2 and $\text{Pd}\cdot\text{SrCO}_3$ in MeOH at 40° , give 3- β -naphthylcyclopentanone-2-acetic acid (I), m.p. 132° (semicarbazone, m.p. 217°), and its *Me* ester, m.p. 79–80°, respectively. (I) and $\text{P}_2\text{O}_5\cdot\text{H}_3\text{PO}_3$ (*d* 1.75) (gentle heating) afford 3':4-diketo-1:2:3:4-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 115° (mono-semicarbazone, m.p. 245°, -hydrazone, m.p. 156°, and -2:4-dinitrophenylhydrazone, m.p. 240°), the constitution of which is confirmed by Clemmensen reduction to an oil, b.p. 200°/1 mm., dehydrogenated ($\text{Pd}\cdot\text{C}$ at 330°) to cyclopentenophenanthrene. The mixed methoxy- and hydroxy-naphthylcyclopentenoneacetic acids (*loc. cit.*) afford *Me* 3- β -6'-methoxy- (II), m.p. 115–116°, and -hydroxy-, m.p. 164–165°, -naphthyl- Δ^2 -cyclopentenone-2-acetate, respectively, but (II) is obtained best by methylating the crude acids before esterification. (II) is hydrogenated to 3- β -6'-methoxynaphthylcyclopentanone-2-acetic acid, m.p. 146–147° (*Me* ester, m.p. 61–62°), which gives [as for (I)] 20% of 3':4-diketo-7-methoxy-1:2:3:4-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 126–127° [2:4-dinitrophenylhydrazone, m.p. 143° (decomp.)]. The latter is reduced (H_2 , $\text{Pt}\cdot\text{C}$, PdCl_2 , EtOH at room temp.) to 3'-keto-7-methoxy-1:2:3:4-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 116–117° [2:4-dinitrophenylhydrazone, m.p. 246–247° (decomp.)]. Qual. experiments with the CHPh and piperonylidene derivatives of the latter support the conclusion that

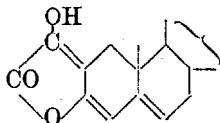
it is α -norequilenin Me ether (α indicating undetermined stereochemical configuration). A. T. P.

isoEquilin-A. H. HIRSCHMANN and O. WINTERSTEINER (J. Biol. Chem., 1938, 126, 737—748).—Equilin with boiling AcOH—conc. HCl in CO₂ yields **isoequilin-A** (I), m.p. 231° (incipient decomp. at 227°, $[\alpha]_D^{25} +222^\circ$ in EtOH [semicarbazone (+0.5H₂O), decomp. 230° (turns brown at 180°)], the acetate, m.p. 95° (softens at 83°), of which with OsO₄ in Et₂O, followed by Na₂SO₃ in 20% EtOH, yields (?) 14-epi- Δ^{9-11} -8-hydroxyequilin, m.p. 204° (decomp.). With Ac₂O in C₅H₅N this gives only a monoacetate (an oil); hence the new OH is probably *tert*. (I) is dehydrogenated (Pd-black) to a compound (? 14-epi-equilenin), C₁₈H₁₈O₂, m.p. 262°, $[\alpha]_D^{25} +160^\circ$ in EtOH, differing from equilenin but having a similar absorption spectrum. From these facts and the nature of the absorption spectrum of (I) and its derivatives, it is concluded that (I) is 14-epi- Δ^{8-9} -equilin, which with OsO₄ gives an osmic ester breaking down with the elimination of H₂O. (I) differs from the diol isolated (A., 1938, III, 299) from the urine of pregnant mares and has about one fifth of the activity of oestrone. All m.p. are corr. A. LI.

Steroids and sex hormones. XLVII. Condensation of cholestenone with oxalic ester. L. RUZICKA and P. A. PLATTNER (Helv. Chim. Acta, 1938, 21, 1717—1725).—Condensation of cholestenone (I) with Et₂C₂O₄ by NaOEt—EtOH and hydrolysis of the product gives **cholestenoneoxalic acid** [(II) R = H], m.p. 150—151°, $[\alpha]_D +38.6^\circ$ in CHCl₃; this gives a dark red colour with FeCl₃ and at 250°/vac. gives (I) in 95% yield. Analogously the non-cryst. Me and Et esters give a large proportion of (I) when heated. With N₂H₄·H₂O in AcOH (II) yields Δ^4 -cholesteno-2':3'-4:5-pyrazole-3-carboxylic acid, m.p. 273—274° (decomp.) (non-cryst. Me ester). (II) is



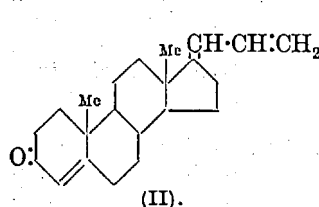
(II.)



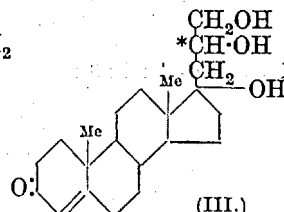
(III.)

transformed by HBr in boiling AcOH into **cholestenoneoxalolactone** (III), m.p. 202° (decomp.), $[\alpha]_D -177^\circ$ in CHCl₃, which is readily autoxidised, does not give a colour with FeCl₃ in EtOH or Et₂O, is completely decomposed when heated, and yields with CH₃N₂ a Me ether, m.p. 137—138°, $[\alpha]_D -214^\circ$ in CHCl₃. Hydrogenation (Pd-sponge in Et₂O) of (II) and treatment of the product with HBr—AcOH gives **dihydrocholestenoneoxalolactone**, m.p. 200° (decomp.), $[\alpha]_D +15.4^\circ$ in CHCl₃ [Me ether, m.p. 137—138°; Ac derivative]. (III) is hydrogenated (Pd-sponge in Et₂O) to **tetrahydrocholestenoneoxalolactone**, m.p. 242° (decomp.), $[\alpha]_D -45.8^\circ$ in CHCl₃ [Me ether, m.p. 133°; acetate, m.p. 183° (decomp.)], oxidised to the acid, C₂₇H₄₆O₄, obtained by Windaus and Ubrig (A., 1914, i, 1066) from cholestanol. (II) and Br react in CHCl₃ to a colourless, non-cryst. product transformed by HBr—AcOH into the **bromolactone**, C₂₉H₄₁O₃Br, m.p. 194° (decomp.) [pyridinium compound, C₃₄H₄₆O₃NBr, m.p. 155° (decomp.)], also obtained by the direct bromination of (III). H. W.

17-Allyltestosterone and its transformation products. A. BUTENANDT and D. PETERS (Ber., 1938, 71, [B], 2688—2695).—Dehydroandrosterone acetate is converted by Mg and CH₂:CH·CH₂Br in Et₂O into 17-allyl- Δ^5 -androstene-3:17-diol, m.p. 151°, $[\alpha]_D^{20} -42.2^\circ$ in EtOH (3-monoacetate, m.p. 154°), transformed by Al(OPrⁱ)₃ and cyclohexanone in boiling PhMe into 17-allyltestosterone (I) (+0.5H₂O), m.p. 105—107.5° or 93° [oxime (+0.5H₂O), m.p. 144—146°]. This is dehydrated by POCl₃ in boiling C₅H₅N to the triene-ketone (II), m.p. 172—174° (semicarbazone, m.p. >365°; darkens slightly ~250°), oxidised by OsO₄ in Et₂O to the corresponding tetrahydroxy-ketone,

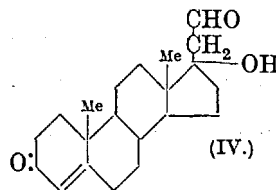


(II.)



(III.)

m.p. 237.5°. (I) is similarly oxidised to the **trihydroxy-ketone** (III), m.p. 224—225°, $[\alpha]_D^{20} +53.9^\circ$, or m.p. 198° (also in a labile form, m.p. 168°), $[\alpha]_D^{20} +48.3^\circ$ (the forms differ from one another only in the steric arrangement around the new asymmetric C*). The first form gives a CPh₃ ether, m.p. 197.5°, whereas the second form does not; the ether is oxidised [Al(OPrⁱ)₃ and cyclohexanone in PhMe] to Δ^4 -androstene-3:17-dione. Oxidation of either form of (III) by Pb(OAc)₄ in C₆H₆ with complete exclusion of air leads to the aldehyde (IV), m.p. 142—143° [dioxime (+1H₂O), m.p. 141° (decomp.) and 208—210° (decomp.) after re-solidifying at about 175—185°]; if air is not excluded the corresponding acid, m.p. 162° (decomp.), is obtained. H. W.



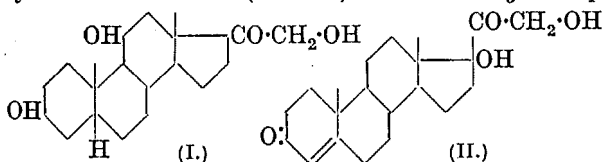
(IV.)

Biochemical transformation of dehydroandrosterone into testosterone.—See A., 1939, III, 55.

Steroids and sex hormones. XLVIII. Conversion of 17-acetylenylandrosterone derivatives into pregnenone derivatives. Preparation of **17-hydroxyprogesterone**. L. RUZICKA and H. F. MELDAHL (Helv. Chim. Acta, 1938, 21, 1760—1770; cf. A., 1938, II, 413).—Addition of 3-trans-17(α)-dihydroxy-17-acetylenyl- Δ^5 -androstene, its 3-acetate (I), or diacetate followed by BF₃—Et₂O to HgO in anhyd. AcOH—Ac₂O gives 3-trans-17(α)-diacetoxy- Δ^5 -pregnen-20-one (II), m.p. 190—192°, $[\alpha]_D^{25} -54^\circ$ in dioxan. (II) does not react with NH₂OH or Girard reagent T; it is hydrolysed (KOH—MeOH) to 3-trans-17(α)-dihydroxy- Δ^5 -pregnen-20-one, m.p. 275—277°, $[\alpha]_D^{25} -110^\circ$ in dioxan [oxime, m.p. 243—244° (decomp.)], converted by Ac₂O in C₅H₅N at room temp. into the 3-acetate, m.p. 270—272°, which could not be acetylated further. (I) is transformed by BzCl in C₅H₅N at 100° into 17(α)-benzoyloxy-3-trans-acetoxy-17-acetylenyl- Δ^5 -androstene, m.p. 209—211°, converted by HgO—AcOH—Ac₂O—BF₃—Et₂O at room temp. into 17(α)-benzoyloxy-3-trans-acetoxy- Δ^5 -pregnen-20-one, m.p. 217—217.5°. Partial hydrolysis (K₂CO₃—

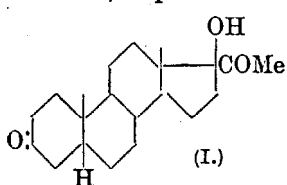
MeOH at room temp.) of (II) and subsequent oxidation (Oppenauer) gives 17-acetoxypregesterone, m.p. 198—200°, $[\alpha]_D^{25} + 68.5^\circ$ in dioxan, hydrolysed to 17-hydroxypregesterone, m.p. 284—288°, $[\alpha]_D^{25} + 54^\circ$ in dioxan (oxime, m.p. 268—270°), also obtained (HgO—AcOH—Ac₂O—BF₃—Et₂O followed by hydrolysis) from 17(α)-acetylenyltestosterone (acetate, m.p. 167—168°). Hydrogenation (PtO₂ in AcOH at room temp.) of (II) gives (?) 3-trans-17(α)-diacetoxypregnan-20-one, m.p. 225.5—227°, $[\alpha]_D^{25} - 4^\circ$ in dioxan, which does not give a yellow colour with C(NO₂)₄. H. W.

Constituents of the adrenal gland. XXI.
Constitution of the substances R and S. T. REICHSTEIN (Helv. Chim. Acta, 1938, 21, 1490—1497; cf. A., 1938, II, 498).—Substance R is (I) since it is oxidised by CrO₃ in AcOH at room temp. to 3:11-diketoalloetiocholic acid and its diacetate, m.p. 172—173° (corr.), is oxidised to the diacetate of compound N. Substance S, obtained by cautious hydrolysis of its acetate (*loc. cit.*) with KHCO₃ in aq.



MeOH at room temp., has m.p. ~210° (corr.; slight decomp.) greatly dependent on the rate of heating and the degree of previous trituration. It is strongly reducing and shows in the ultra-violet absorption spectrum the bands typical of αβ-unsaturated ketones. Oxidation of it with CrO₃ in AcOH at room temp. yields Δ⁴-androstene-3:17-dione. S is therefore (II) if the possibility of the presence of the group :C(OH)-CH(OH)-CHO is disregarded. The sole uncertainty is the configuration at C₍₁₇₎. H. W.

Constituents of the adrenal gland. XXII.
Constitution of substance L. T. REICHSTEIN and K. GÄTZI (Helv. Chim. Acta, 1938, 21, 1497—1505; cf. A., 1936, 1382).—Substance L, m.p. 264—266° (corr.), $[\alpha]_D^{25} + 30.6^\circ \pm 3^\circ$ in abs. EtOH, as obtained by various enrichment processes, is best purified by taking advantage of its sparing solubility in boiling C₆H₆ and then through the acetate. Ac₂O and C₆H₅N at room temp. transform crude L into the L-acetate, m.p. 191—192° (corr.), $[\alpha]_D^{25} + 14.8^\circ \pm 2^\circ$ in COMe₂, which appears to be a mixture of Ac₁ and Ac₂ derivatives, and a second acetate, m.p. 182—182.5° (corr.), $[\alpha]_D^{25} + 19.3^\circ \pm 2^\circ$ in COMe₂ [semi-carbazone, m.p. 255—259° (corr.)], which appears to be the Ac₂ derivative of a compound, C₂₁H₃₄O₃. L does not reduce Ag₂O solution and does not give the absorption bands typical of αβ-unsaturated ketones. It is oxidised by CrO₃ in AcOH at room temp. to



a substance (I), m.p. 270—272° (corr.), and androstane-3:17-dione. Reduction (Raney Ni) of L gives a mixture of two stereoisomeric triols readily separated through their diacetates and recognised as substances J and O. L is therefore (I) with CO=CH-OH. L, J, and O have therefore the same configuration at

E* (A., II.)

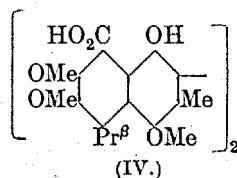
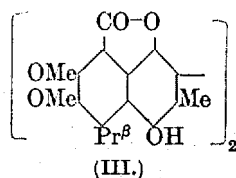
C₍₁₇₎ and the main difference between J and O is due to the different spatial arrangement of OH at C₍₂₀₎. H. W.

[Interaction of] phenols and sulphites. (MILLER.) Y. GARREAU (Ann. Chim., 1938, [xi], 10, 485—558).—Mainly a comprehensive account of work already reported (A., 1935, 245, 348; 1936, 337, 721; 1937, II, 66, 251, 338; 1938, II, 96, 136, 237).—When quinol (0.2 mol.) is shaken in air with aq. SO₂ (1 mol.), NH₃ or NH₂Alk (3 mols.), and Cu(OH)₂ (0.05 mol.) (indispensable for good yields), there are obtained 2:5-diamino-1:4-benzoquinone-3- and -3:6-disulphonic acids and 2(or 5)-amino-5(or 2)-hydroxy-1:4-benzoquinone-4-imine-3- and -3:6-di-sulphonic acids (or their alkylamino-homologues), the nature of the product(s) depending mainly on the nature of the base, but in some cases also on the conditions. Occurrence of hydrolysis of the SO₃H by AcOH or dil. HCl depends remarkably on the nature of the basic substituents. The following appear new. 2:5-Di-n-butyl-, m.p. 160°, -diisobutyl-, m.p. 197°, -di-n-amyl-, m.p. 143°, and -diisoamyl-amino-1:4-benzoquinone, m.p. 170°. Diisobutylammonium 2:5-diisobutyl-, di-n-amylammonium 2:5-di-n-amyl-, and diisoamylammonium 2:5-diisoamyl-amino-1:4-benzoquinone-3:6-disulphonate. β-Hydroxyethylammonium (? 2:5-) di-(β-hydroxyethylamino)-1:4-benzoquinone-3-sulphonate, +2H₂O. R. S. C.

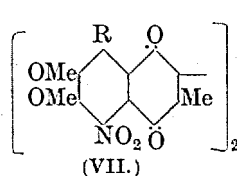
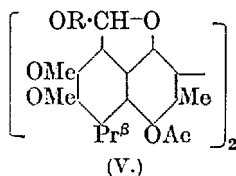
Action of diazonium compounds on 2-hydroxy-1:4-naphthaquinone. O. NEUNHOEFFER and J. WEISE (Ber., 1938, 71, [B], 2703—2707).—In AcOH 2-hydroxy-1:4-naphthaquinone (I) couples with diazo-compounds exclusively to azo-dyes, whereas in alkaline solution N₂ is eliminated with production of an arylated hydroxynaphthaquinone. Addition of o-C₆H₄Me-N₂Cl to a solution of (I) in 5% KOH at 45° gives 2-hydroxy-3-o-tolyl-1:4-naphthaquinone, m.p. 127° (monoacetate, m.p. 76°), converted by heating with Zn dust and Ac₂O containing a trace of H₂SO₄ into 1:2:4-triacetoxy-3-o-tolynaphthalene, m.p. 132°. The following compounds are obtained analogously: 2-hydroxy-3-phenyl-1:4-naphthaquinone m.p. 146°, and 1:2:4-triacetoxy-3-phenyl-naphthalene, m.p. 168°; 2-hydroxy-3-p-tolyl-1:4-naphthaquinone, m.p. 168° (acetate, m.p. 138—139°), and 1:2:4-triacetoxy-3-p-tolynaphthalene, m.p. 188°; 2-hydroxy-3-β-naphthyl-1:4-naphthaquinone, m.p. 195° (monoacetate, m.p. 156°); 2-hydroxy-3-p-anisyl-1:4-naphthaquinone, m.p. 127°, and its acetate, m.p. 121.5°; 2-hydroxy-3-o-carboxyphenyl-1:4-naphthaquinone, m.p. 248°, and the corresponding lactone, C₁₇H₈O₄, m.p. 253° (decomp.); 2-hydroxy-3-p-carboxyphenyl-1:4-naphthaquinone, m.p. 288° [monoacetate (+0.5H₂O)]; the K salt (+0.5H₂O) of 2-hydroxy-3-p-sulphophenyl-1:4-naphthaquinone. H. W.

Structure of gossypol. XVI. Reduction products of gossypolone tetramethyl ether and gossypolonic acid tetramethyl ether. XVII. Nitration of gossypol hexamethyl ether, gossypolone tetramethyl ether, and gossypolonic acid tetramethyl ether. R. ADAMS, T. A. GEISSMAN, and R. C. MORRIS. XVIII. Synthesis of 3:4-dimethoxy-5-isopropylaniline. R. ADAMS, M. HUNT,

and R. C. MORRIS (J. Amer. Chem. Soc., 1938, 60, 2967—2970, 2970—2972, 2972—2974).—XVI. The quinone structure of gossypolonic acid Me_4 ether (I) and gossypolone Me_4 ether (II) (A., 1938, II, 452) is proved by reduction. With Zn dust in boiling AcOH (I) gives *hydroxygossypolactone* Me_4 ether (III), m.p. 320° (block), and in Ac_2O its Ac_2 derivative, m.p. 231 — 233° , also obtained from (III) by Ac_2O — $\text{C}_5\text{H}_5\text{N}$. With Me_2SO_4 in KOH — MeOH (III) gives its Me_2 [*hydroxygossypolactone* Me_6] ether, m.p. 273 — 274° , hydrolysed by warm KOH — MeOH in presence of a little Zn dust to *methoxygossylic acid* Me_4 ether (IV), m.p. 250° (preheated bath), which is re-converted into the lactone at the m.p. or by warm Ac_2O . Reduction of (II) is difficult owing to the



instability of the product, but $\text{Na}_2\text{S}_2\text{O}_4$ in hot abs. EtOH , followed by Ac_2O — $\text{C}_5\text{H}_5\text{N}$, gives the *acetal* [(V) $\text{R} = \text{Et}$], m.p. 264 — 265° , and in MeOH the *compound*, [(V) $\text{R} = \text{Me}$], m.p. 266 — 267° , is formed. CrO_3 oxidises [(V) $\text{R} = \text{Me}$ or Et] to (II). In MeOH —



KOH (III) is hydrolysed, oxidised, and then degraded. Prep. of gossypol Me_6 ether (VI) is improved.

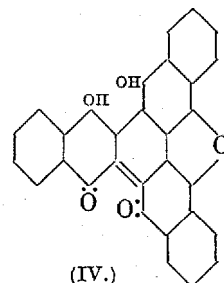
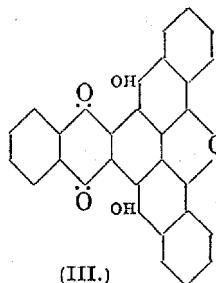
XVII. With HNO_3 (d 1.5) at -5° (VI) or (II) suffers replacement of Pr^6 by NO_2 , giving the *compound* [(VII) $\text{R} = \text{CHO}$], decomp. 257 — 262° (darkens at 220°) (*dianil*, darkens at $\sim 210^\circ$, chars at $\sim 260^\circ$). With HNO_3 (d 1.5) (I) gives similarly the *acid* [(VII) $\text{R} = \text{CO}_2\text{H}$], darkens 260 — 270° (begins at $\sim 220^\circ$), m.p. $>320^\circ$ (block), also obtained from [(VII) $\text{R} = \text{CHO}$] by HNO_3 .

XVIII. $3:4:5:1\text{-(OMe)}_2\text{C}_6\text{H}_2\text{Pr}^6\text{-NH}_2$ is synthesised. Its identity with the base obtained by degradation of gossypol (*loc. cit.*) proves the presence of Pr^6 , the position of the OH relative thereto, and thus, in conjunction with other evidence, the 1-, 5-, 6-, 7-, and 8-substituents. Dry $o\text{-OMe-C}_6\text{H}_4\text{ONa}$ and CO_2 at 115° give 33% of $3:2:1\text{-OMe-C}_6\text{H}_2(\text{OH})\text{-CO}_2\text{H}$, m.p. 150° , the Me ester, m.p. 61° (lit., 63°), b.p. 134 — $136^\circ/2\text{ mm.}$, of which with MgMeCl gives *2-hydroxy-3-methoxyphenyldimethylcarbinol*, m.p. 126° , dehydrated at 195 — 200° to *2-hydroxy-3-methoxyisopropenylbenzene*, b.p. 122 — $124^\circ/14\text{ mm.}$ H_2 —Raney Ni in 95% EtOH at 2—3 atm. then gives *2-hydroxy-3-methoxyisopropylbenzene*, b.p. 123 — $125^\circ/8\text{ mm.}$, converted (Me_2SO_4) into *2:3-dimethoxyisopropylbenzene*, b.p. 119 — $121^\circ/24\text{ mm.}$, which with HNO_3 (d 1.5) in AcOH yields the 5-NO_2 , m.p. 53° , or $(\text{NO}_2)_2$ -derivative, m.p. 106° , and thence (H_2 , Raney Ni, EtOH) *3:4-dimethoxy-5-isopropylaniline*, m.p. 75°

(Ac_2 derivative, m.p. 86°), and a $(\text{NH}_2)_2$ -derivative, m.p. 75° , respectively. M.p. (all parts) are corr.

R. S. C.

Polymerisation processes. Condensation of 1:4-naphthaquinone to triphthalylbenzene by pyridine. R. PUMMERER, A. LÜTTRINGHAUS, R. FICK, A. PFAFF, G. RIEGELBAUER, and E. ROSENHAUER (Ber., 1938, 71, [B], 2569—2583; cf. A., 1938, II, 65).—The yellow condensation product from 1:4-naphthaquinone (*loc. cit.*; G.P. 350,783) is not dinaphthylenediquinone but triphthalylbenzene (I). It is converted by the successive action of NaOH — $\text{Na}_2\text{S}_2\text{O}_4$ and $o\text{-C}_6\text{H}_4\text{Cl-COCl}$ into *hexahydrotriphthalylbenzene hexa-o-chlorobenzoate* (II), m.p. 240 — 242° (decomp.) after softening at 180° . The green anhydroquinhydrone of (I) is (III) or (IV) since it yields a *diacetate*, m.p. 325° (decomp.), a *di-o-chlorobenzoate*, m.p. 317° , and is converted by $\text{Na}_2\text{S}_2\text{O}_4$ — NaOH followed by $o\text{-C}_6\text{H}_4\text{Cl-COCl}$ into the *tetra-o-chlorobenzoate*, m.p. 325 — 330° after softening, of the dihydroanhydroquinhydrone. (I) is reduced by Zn dust at incipient redness to the hydrocarbon (V), $\text{C}_{30}\text{H}_{18}$, m.p. 392° (corr.), also obtained similarly or



by use of 48% HI at 200° from (III) or (IV). (I) is oxidised by 91% HNO_3 at 130° to mellitic acid. (I) is transformed by NaOH — $\text{Na}_2\text{S}_2\text{O}_4$ and treatment of the product by air into a red substance, oxidised (65% HNO_3 at 160 — 165°) to $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$.

The constitution of (V) as tri-2:3-naphthylene is confirmed by the determination of its mol. wt. in boiling PhCl ; its picrate (*cf. loc. cit.*) therefore has its components in the ratio 1:1, not 3:2. The mol. wt. of (II) has been determined similarly. The substance obtained by reduction of (I) with HI and red P is identified as *tetracosihydrotrinaphthylene*, m.p. 360 — 362° after softening.

The "triphthalylbenzene" of Scholl *et al.* (A., 1937, II, 34), obtained in minimal yield by heating 2:3-dichloro-1:4-naphthaquinone with Cu powder, is very probably *di-2-naphthaquinonylnaphthaquinone*. Reductive acetylation appears to give the *tetraacetate*, m.p. 325° (decomp.), of a H_4 -derivative.

H. W.

Preparation and properties of pure ionene. A. MÜLLER (J. pr. Chem., 1938, [ii], 151, 249—250).—Ionene, b.p. 238 — $239^\circ/730\text{ mm.}$, is obtained pure by threefold treatment of α -ionone with Na and I followed by distillation over Na under atm. pressure. In contrast with β -ionone it does not give an intensely coloured condensation product with the usual $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$ reagent but yields a yellow-red to Bordeaux-red colour if the $[\text{H}_3\text{PO}_4]$ is increased.

H. W.

Preparation of N-methylmenthylamines by a new method of N-alkylation. J. READ and J. A. HENDRY (Ber., 1938, 71, [B], 2544—2552).—Reactions follow the scheme: $\text{NH}_2\text{R} + \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et} \rightarrow \text{NHR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \rightarrow \text{NHR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{NHRMe} + \text{CO}_2$. *sec.* Amines can be used similarly. Thus *l*-menthylaminoacetic acid gives *N*-methyl-*l*-menthylamine (I), b.p. 87°/12 mm., $[\alpha]_D^{25} -78.27^\circ$ (homogeneous), $[\alpha]_D^{25} -69.2^\circ$ in CHCl_3 (hydrochloride, m.p. 168°, $[\alpha]_D^{25} -52.75^\circ$ in H_2O ; Bz, m.p. 65°, $[\alpha]_D^{25} -32.4^\circ$ in CHCl_3 , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$, m.p. 61°, $[\alpha]_D^{25} -37.5^\circ$ in CHCl_3 , derivatives; *N*-methyl-*l*-menthynitrosoamine, m.p. 30.5°, $[\alpha]_D^{25} -39.5^\circ$ in CHCl_3 , -54.0° in C_6H_6), with some 2 : 5-diketo-1 : 4-di-*l*-menthyllpiperazine, m.p. 201—202° (decomp.), $[\alpha]_D^{25} -106.3^\circ$ in CHCl_3 . (I) is transformed by $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and subsequent hydrolysis into *l*-menthylmethylaminoacetic acid (+ H_2O), m.p. 148°, $[\alpha]_D^{25} -51.5^\circ$ in H_2O , whence *l*-menthyl-dimethylamine (II), b.p. 90.5°/10 mm., $[\alpha]_D^{25} -60.50^\circ$ (homogeneous), $[\alpha]_D^{25} -59.7^\circ$ in CHCl_3 [platinichloride, m.p. 205—206° (decomp.)]. *l*-Menthyltrimethylammonium iodide, m.p. 190° (decomp.), $[\alpha]_D^{25} -39.3^\circ$ in H_2O , passes at 190°/atm. pressure into (II) and menthene, $[\alpha]_D^{25} +75.24^\circ$ (homogeneous); when treated with Ag_2O and distilled at 165—170°/10 mm., the products are (II) and a menthene, b.p. 56°/10 mm., $\alpha_D^{25} +107.34^\circ$ ($l=1$; homogeneous), $[\alpha]_D^{25} +131.7^\circ$ (homogeneous), $[\alpha]_D^{25} +149.7^\circ$ in abs. EtOH, $+149.2^\circ$ in Et₂O. Et neomenthylaminoacetate is hydrolysed to *d*-neomenthylaminoacetic acid, m.p. 182°, $[\alpha]_D^{25} +28.1^\circ$ in H_2O , $+32.2^\circ$ in abs. EtOH, which passes when heated into 2 : 5-diketo-1 : 4-di-*d*-neomenthyllpiperazine, m.p. 63°, $[\alpha]_D^{25} +43.9^\circ$ in CHCl_3 (hydrochloride, m.p. 242°, $[\alpha]_D^{25} +42.9^\circ$ in CHCl_3), and *N*-methyl-*d*-neomenthylamine, b.p. 87°/12 mm., $[\alpha]_D^{25} +20.44^\circ$ (homogeneous), $+26.4^\circ$ in CHCl_3 (hydrochloride, m.p. 196°, $[\alpha]_D^{25} +16.7^\circ$ in H_2O ; Bz, m.p. 67°, $[\alpha]_D^{25} +5.7^\circ$ in CHCl_3 , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$, m.p. 49°, $[\alpha]_D^{25} +18.5^\circ$ in CHCl_3 , derivatives; *N*-methyl-*d*-neomenthynitrosoamine, m.p. 62°, $[\alpha]_D^{25} +19.9^\circ$ in CHCl_3). *N*-Methyl-*d*-neomenthylaminoacetic acid, m.p. 98° or (+ $2\text{H}_2\text{O}$) m.p. 55°, $[\alpha]_D^{25} +28.5^\circ$ in H_2O , passes at 200° into CO_2 , NHMe_2 , *d*- Δ^3 -menthene, b.p. 70°/15 mm., $[\alpha]_D^{25} +102.2^\circ$ (homogeneous), and *d*-neomenthyldimethylamine, b.p. 93°/12 mm., $[\alpha]_D^{25} +42.69^\circ$ (homogeneous), $+40.7^\circ$ in CHCl_3 [platinichloride, m.p. 196° (decomp.)]; hydrochloride, $[\alpha]_D^{25} +15.3^\circ$ in H_2O . *d*-Neomenthyltrimethylammonium iodide, m.p. 160.5° (decomp.), $[\alpha]_D^{25} -19.5^\circ$ in H_2O (corresponding tri-iodide, m.p. 107°), passes at 155—160°/20 mm. into NMe_3 , HI, and *d*- Δ^3 -menthene, b.p. 59°/10 mm., $\alpha_D^{25} +80.66^\circ$ ($l=1$; homogeneous). The cryst., very hygroscopic *d*-neomenthyltrimethylammonium hydroxide is converted at 150—160°/15 mm. or at 175—180°/atm. pressure into H_2O , NMe_3 , and *d*- Δ^3 -menthene, b.p. 57°/10 mm., $[\alpha]_D^{25} +112.9^\circ$ (homogeneous), $[\alpha]_D^{25} +108.5^\circ$ in abs. EtOH, $+112.9^\circ$ in Et₂O. NH_2Ph is converted into anilinoacetic acid, m.p. 126—127°, which, at 200°, gives mainly 2 : 5-diketo-1 : 4-diphenylpiperazine, m.p. 263°, with a smaller proportion of NHPhMe . $\text{NPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ readily decomposes when heated into NPhMe_2 and CO_2 . Addition of Na_2CO_3 , NaOAc , $\text{C}_5\text{H}_5\text{N}$, quinoline, or NPhMe_2 to the mixture of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and amine (to absorb the liberated HCl) is disadvantageous. H. W.

***l*-Menthyl dialkylbetaine acetates.** (MME.) Y. RIGHETTI (Bull. Soc. chim., 1938, [v], 5, 1463—1472; cf. (Mme.) Guaisnet-Pilaud, A., 1936, 196).—*l*-Menthyl-dimethylamino-, (I), b.p. 140.5—141°/14—15 mm., -methylethylamino- (II), b.p. 151—155°/17 mm., -methylpropylamino- (III), b.p. 166°/20 mm., and -dipropylamino-, b.p. 172.5—173.5°/13 mm., -acetate are prepared from *l*-menthyl bromoacetate (IV) and the corresponding amine in Et₂O. (I) and (IV) afford bis-(*l*-menthyl acetate)dimethylammonium bromide, $\text{N}(\text{CH}_2\cdot\text{CO}_2\text{C}_{10}\text{H}_{19})_2\text{Me}_2\text{Br}$, in a form converted at 80° or slowly by H_2O into a form, m.p. 127—128° (decomp.); each with Ag_2O —EtOH gives the betaine, $\text{CO} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{NRR}'\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_{10}\text{H}_{19}$ [(A), R = R' = Me] (+ $3\text{H}_2\text{O}$, lost at 100°; anhyd., m.p. 198—199° (decomp.), $[\alpha]_D^{25} -50.43^\circ$ in EtOH. The cryst. quaternary bromides from *l*-menthyl-diethyl- and -dipropylaminoacetates and (IV)— Ag_2O give the corresponding betaines. The stable quaternary bromide from (II) and (IV), or from (II) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (in this case a little inactive Ag salt of the betaine is isolated), or from (IV) and Et methylethylaminoacetate, give betaines [(A); R = Me, R' = Et], a monohydrate, m.p. 162° (V), $[\alpha]_D^{25} -42.4^\circ$ in EtOH, and a geometrical isomeride in anhyd. form (VI), m.p. 175°, $[\alpha]_D^{25} -50^\circ$ in EtOH. (VI) and dil. HCl— Ag_2O give (V). The stable quaternary bromides from (III) or the benzylmethyl analogue, with (IV), give betaines with difficulty. A. T. P.

Mixed ethyl *l*-menthyl dilactylates [oxidodi- $\alpha\alpha$ -propionic acid derivatives]; attempt to prepare an optically active diester. M. GODCHOT and P. VIÈLES (Bull. Soc. chim., 1938, [v], 5, 1535—1539; cf. A., 1932, 253; 1935, 474).— $\text{CHMeBr}\cdot\text{COBr}$ and *l*-menthol in Et₂O give *l*-menthyl (*d* + *l*)- α -bromopropionate, b.p. 156—160°/15 mm., which with (*d* + *l*)-Et lactate, $\alpha_{468}^{25} -0.04^\circ$, gives a mixture, b.p. 134—138°/20 mm., $[\alpha]_D^{25} -11.2^\circ$, of (*d* + *l*) and (*i*)-dilactylates of Et and *l*-menthyl, hydrolysed, with isomerisation of latter, by excess of NaOH—EtOH to a Na_2 dilactylate, $\alpha 0^\circ$. A. T. P.

Terpene ethers.—See B., 1939, 18.

Addition reactions to conjugated systems.
 β -Phellandrene and maleic anhydride. N. F. GOODWAY and T. F. WEST (J.C.S., 1938, 2028—2031).—Pure *l*- β -phellandrene and maleic anhydride (I) give a resinous product, containing a small quantity of adduct identical with that obtained from *l*- α -phellandrene. The available evidence indicates that the *l*- β -phellandrene-(I) adduct is derived from β -phellandrene and (I) by thermal decomp. of the primary resinous product. The bearing of this result on the stereochemistry of more complex structures is discussed. F. R. S.

Thujone series. I. Thujones and some thujyl alcohols and thujylamines. A. G. SHORT and J. READ (J.C.S., 1938, 2016—2021).—The stereochemical relationship of the so-called " α -thujone" of thuja oil to " β -thujone" of tansy oil is similar to that of *l*- to *d*-iso-menthone. *l*-Thujone, obtained by oxidation (CrO_3) of *l*-thujyl alcohol, has b.p. 74.5°/9 mm., $\alpha_D^{25} -19.94^\circ$ ($l=1$), and forms a 2 : 4-dinitrophenyl-

hydrazone, m.p. 117° , $[\alpha]_D^{10} +44.0^{\circ}$ in CHCl_3 . *d*-iso-Thujone, similarly prepared from *d*-isothujyl alcohol, has b.p. $76^{\circ}/10$ mm., $[\alpha]_D^{15} +72.46^{\circ}$, and gives a 2:4-dinitrophenylhydrazone, m.p. 116° , $[\alpha]_D^{15} +161^{\circ}$ in CHCl_3 . In presence of NaOEt-EtOH , the isomerides undergo interconversion, the equilibrium mixture containing 35% of *l*-thujone. Hydrogenation of " α -" or " β -thujone" in C_6H_{12} with a catalyst yields *l*-thujyl alcohol, m.p. $66-67^{\circ}$, $[\alpha]_D^{15} -20.5^{\circ}$ in MeOH (*p*-nitrobenzoate, m.p. 101° , $[\alpha]_D^{15} -32.25^{\circ}$ in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 106° , $[\alpha]_D^{15} -24.5^{\circ}$ in CHCl_3). Reduction of " α -" or " β -thujone" with Na-EtOH gives *d*-isothujyl alcohol, b.p. $103^{\circ}/16$ mm., $\alpha_D^{14} +106.70^{\circ}$ (3:5-dinitrobenzoate, m.p. 92° , $[\alpha]_D^{15} +96.75^{\circ}$ in CHCl_3 ; *p*-nitrobenzoate, m.p. 78° , $[\alpha]_D^{15} +107.0^{\circ}$ in CHCl_3). Crude *l*-thujone oxime is reduced (Na-EtOH) to *l*-thujylamine, b.p. $81.5^{\circ}/15.5$ mm., $\alpha_D^{15} -24.32^{\circ}$ [hydrochloride, m.p. $248-249^{\circ}$ (decomp.), $[\alpha]_D^{16} -15.75^{\circ}$ in H_2O ; *p*-nitrobenzoyl, m.p. 146.5° , $[\alpha]_D^{16} -51.25^{\circ}$ in CHCl_3 , and *salicylidene* derivatives, m.p. 66° , $[\alpha]_D^{15} -7.03^{\circ}$ in CHCl_3 ; *l*-thujyltrimethylammonium iodide, m.p. 269° (decomp.), $[\alpha]_D^{15} -30.75^{\circ}$ in CHCl_3 ; picrate of *N*-dimethyl-*l*-thujylamine, m.p. $137-138^{\circ}$, $[\alpha]_D^{15} -40.5^{\circ}$ in CHCl_3]. Similarly *d*-isothujylamine has b.p. $75.5^{\circ}/11$ mm., $\alpha_D^{13} +94.82^{\circ}$, and forms benzoyl, m.p. 131.5° , $[\alpha]_D^{15} +90.5^{\circ}$ in CHCl_3 and *p*-nitrobenzoyl derivatives, m.p. 147° , $[\alpha]_D^{15} +77.0^{\circ}$ in CHCl_3 , *d*-isothujyltrimethylammonium iodide, m.p. 260° (decomp.), $[\alpha]_D^{15} +47.0^{\circ}$ in CHCl_3 , and the *platini*-chloride of *N*-dimethyl-*d*-isothujylamine, m.p. $173-174^{\circ}$ (decomp.). A mixture of *d*thujylamines, b.p. $181-182^{\circ}/9$ mm., $\alpha_D^{14} +23.5^{\circ}$, is obtained from " α -thujone" and HCO_2NH_4 , followed by MeOH-HCl . A similar mixture of *d*imethylamines, b.p. $176^{\circ}/10$ mm., $\alpha_D^{15} -9.96^{\circ}$, is obtained from *l*-menthone and HCO_2NH_4 . F. R. S.

Triterpene group. IV. Triterpene alcohols of Taraxacum root. S. BURROWS and J. C. E. SIMPSON (J.C.S., 1938, 2042-2047).— Al_2O_3 adsorption of the non-saponifiable matter of the root shows the complexity of the mixture. The "*homotaraxasterol*" of Power and Browning (J.C.S., 1912, 101, 2411) is a mixture. Seven compounds have been isolated: taraxasterol (*p*-nitrobenzoate, m.p. $277-278^{\circ}$, $[\alpha]_D^{17} +98.3^{\circ}$) is a chemical individual, and is oxidised ($\text{CrO}_3\text{-AcOH}$) to a product, $\text{C}_{30}\text{H}_{48}\text{O}$, m.p. $175-176^{\circ}$, $[\alpha]_D^{15} +109.5^{\circ}$; β -amyryn, isolated as the acetate; stigmasterol; β -sitosterol; taraxol, $\text{C}_{30}\text{H}_{46}\text{O}_3$, m.p. $>360^{\circ}$, $[\alpha]_D^{14} +78.6^{\circ}$ [acetate, m.p. $299-301^{\circ}$ (decomp.), $[\alpha]_D^{14} +93.9^{\circ}$; oxide acetate, m.p. $294-297^{\circ}$; oxide, m.p. $261-261.5^{\circ}$]; taraxerol, $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. $269-271^{\circ}$ (benzoate, m.p. $282-284^{\circ}$, $[\alpha]_D^{15} +35.0^{\circ}$; acetate, m.p. $296-297^{\circ}$, $[\alpha]_D^{15} +8.4^{\circ}$); and ψ -taraxasterol, m.p. $198-200^{\circ}$, $[\alpha]_D^{15} +47.1^{\circ}$ (benzoate, m.p. $274-276^{\circ}$, $[\alpha]_D^{15} +72.3^{\circ}$; acetate, m.p. $234-235.5^{\circ}$, $[\alpha]_D^{15} +53.2^{\circ}$). The physical consts. of taraxasterol, the three new alcohols, and their derivatives indicate their probable triterpenoid nature. All rotations are in CHCl_3 . F. R. S.

Structure of triterpenes. L. RUZICKA and W. J. SMITH (Chem. and Ind., 1938, 1210-1211).—The hydrocarbon, m.p. $128-129^{\circ}$ (picrate, m.p. $167-168^{\circ}$; quinone, m.p. $207-208^{\circ}$; quinoxaline derivative, m.p. $182-183^{\circ}$), obtained from hederagenin or

basseol by Se, is shown by synthesis (not detailed) to be 1:2:6-trimethylphenanthrene. This confirms Ruzicka's structure for basseol (A., 1934, 530) and is in line with various formulæ proposed for β -amyryn.

R. S. C.

Lignin. XIX. Derivatives of pine lignin containing mercury and iodine. K. FREUDENBERG and H. F. MÜLLER (Ber., 1938, 71, [B], 2500-2504).—In reply to the criticism of Hilpert *et al.* (A., 1937, II, 205) on the work of Freudenberg *et al.* (A., 1931, 1278), the mercuration of methyl-lignin (I) has been effected with addition of AcOH during the boiling and with washing of the products with the acid. The observation that a limiting val. for the entering Hg is attained and cannot be exceeded is proof that there is a true reaction between (I) and $\text{Hg}(\text{OAc})_2$. Contrary to Hilpert, the differences in the reactivity of the metal in the Hg compounds of (I), vanillin, and homoveratrole are not such as to justify the assumption that it is in different types of union. Observations on the iodo-compounds, readily obtained from the Hg compound by I-KI , show that Hg is contained in large amount in (I) and that the reaction is concerned with substituents in C_6H_6 nuclei; I is retained with a firmness which with infrequent exceptions is found only in derivatives of PhI . H. W.

Chlorine-sodium sulphite reaction of woody tissues and the constitution of hardwood lignin.—See A., 1939, III, 217.

Methylation of ursolic acid. H. M. SELL and R. E. KREMERS (J. Biol. Chem., 1938, 126, 501-503; cf. Jacobs *et al.*, A., 1931, 1154).—Pure ursolic acid with CH_2N_2 or Me_2SO_4 , or Ag ursolate with MeI , gives (good yield) only one Me ester, m.p. $170-171^{\circ}$. A. LI.

Ether-soluble constituents of sarsaparilla root. II. J. C. E. SIMPSON and N. E. WILLIAMS (J.C.S., 1938, 2040-2042; cf. A., 1937, II, 289).—The liquid fraction of the unsaponifiable matter obtained from the Et_2O -sol. material consists of a highly complex mixture of unsaturated alcohols and hydrocarbons, probably containing azulene. Treatment of two of the more volatile fractions with 3:5- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{-COCl}$ gives traces of a substance, $\text{C}_{15}\text{H}_{11}\text{O}_6\text{N}_2$, m.p. 111° . An alcohol, $\text{C}_6\text{H}_{12}\text{O}$, has been isolated as its pyruvic ester semicarbazone, m.p. $114-115^{\circ}$, and also an alcohol, $\text{C}_{18}\text{H}_{36}\text{O}$, as the pyruvic ester semicarbazone, m.p. $137-137.5^{\circ}$. F. R. S.

Egonol. V. Nature of the hydroxyl group of egonol and the oxidation of acetylegonol by selenium dioxide. S. KAWAI and K. YAMAGAMI. VI. Optical activity and active hydrogen atoms of egonol. S. KAWAI and N. SUGIYAMA (Ber., 1938, 71, [B], 2438-2443, 2443-2447; cf. A., 1938, II, 501; 1939, II, 32).—V. Egonol (I) and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ in boiling PhMe yield egonol *H phthalate* (II), m.p. $153-153.5^{\circ}$ (Ag salt, m.p. 177°); the OH of (I) is very probably primary. Oxidation of acetylegonol by SeO_2 in Ac_2O yields α -di(acetylegonolyl) selenide (III), $\text{C}_{42}\text{H}_{38}\text{O}_{12}\text{Se}$, m.p. $159-160^{\circ}$, nor-egonolonidine acetate, m.p. $180-180.5^{\circ}$, and β -di(acetylegonolyl) selenide (IV), m.p. $150-150.5^{\circ}$. (III) is hydrolysed (KOH-MeOH) to α -diegonolyl selenide,

m.p. 224—225° (*di-p-nitrobenzoate*, m.p. 186—188°). (IV) gives β -*diegonolyl selenide*, m.p. 174—175°.

VI. Egonoké oil, obtained by cold pressing, is hydrolysed by the requisite amount of KOH in cold $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{OMe}$ and (I) thus obtained is crystallised repeatedly from aq. COMe_2 and then from aq. MeOH, whereby an optically inactive product is ultimately obtained; this does not give a ppt. with digitonin. The optical activity of the oil is due to the presence of phytosterol. (II) does not give well-cryst. salts with brucine, strychnine, or cinchonine. 1-*Brucine styrazinolate*, decomp. 212.5—213°, $[\alpha]_D^{20} + 16.97^\circ$ in CHCl_3 , give optically inactive styrazinolic acid (IV) when decomposed by NH_3 . It cannot be maintained that (I) and (IV) do not contain an asymmetric C since H at C_{41} is readily mobile and hence asymmetric C_{41} would be readily racemised. By use of MgMeI in $\text{C}_5\text{H}_5\text{N}$ it is shown that (I) and its Ac derivative contain 2 and one active H respectively. Under similar conditions the expected no. of active H are found in *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, xanthhydrol, and *p*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{Ac}$ whereas 2 active H are present in $\text{CH}_2(\text{CO}_2\text{Et})_2$ and there is none in CH_2Ph_2 . Since the use of MgMeI or MgEtBr shows the presence of 1 active H in cyclopentadiene, indene, or fluorene, it must be admitted that (I) contains 2 active H of which one is united directly to C. H. W.

Catuabol obtained from the bark of catuabach (*Trichilia spec.*). M. M. JANOT and E. CRONGA (Compt. rend., 1938, 207, 798—799).—Cold EtOH extracts a material from which C_6H_6 removes a substance, m.p. 115—116°, and *catuabol* (I), $\text{C}_{25}\text{H}_{40}\text{O}$, m.p. 200—201° (block), $[\alpha]_D^{18} + 88.4^\circ$ in CHCl_3 (*formyl*, *Ac*, and *Bz* derivatives, m.p. 242—243°, 242—243°, and 235—236°, respectively), which does not react with Br, $\text{KMnO}_4 \cdot \text{COMe}_2$, $\text{C}(\text{NO}_2)_4 \cdot \text{CHCl}_3$, or FeCl_3 . (I) contains a labile H but no OMe or OEt. (I) with $\text{CrO}_3 \cdot \text{AcOH}$ affords a ketone (*oxime*, m.p. 238—240°). J. L. D.

African arrow poisons. II. Heart poisons in Calotropis sap. G. HESSE, F. REICHENEDER, and H. EYSENACH (Annalen, 1938, 537, 67—86; cf. A., 1937, II, 71).—Coagulation of the sap by EtOH and treatment of the aq.-alcoholic serum by the method used previously (*loc. cit.*) does not yield calotropin (I) but a no. of new poisons, of which *uscharin* (II), *calotoxin* (III), and *calactin* (IV) are described. (II), decomp. 265° or higher if heating is rapid, $[\alpha]_D + 29.0^\circ$ in CHCl_3 , is $\text{C}_{31}\text{H}_{41}\text{O}_8\text{NS}$. It gives compounds $+1\text{H}_2\text{O}$, $+1\text{EtOH}$, and $+1$ or 2 mols. of dioxan. It gives a positive Legal test and darkens boiling plumbite solution. (II) is readily decomposed by boiling dil. acids to NH_3 , volatile org. compounds containing S, and *uscharidin* (V), $\text{C}_{29}\text{H}_{40}\text{O}_9$, decomp. 290° (also *monohydrate*). It is isomeric with (I). It is converted by $\text{NH}_2\text{OH} \cdot \text{HCl}$ and NaOAc in boiling EtOH into *uscharidin-oxime*, decomp. 257°, also obtained similarly from (II). With CH_2N_2 in $\text{MeOH} \cdot \text{Et}_2\text{O}$ (V) gives *methyluscharidin*, decomp. 224°. Catalytic hydrogenation (Pb in EtOH) of (V) slowly gives *dihydro-uscharidin*, decomp. 200°, which gives a positive Legal reaction. Hydrogenation (PtO_2 in AcOH) of (V) causes absorption of nearly 2H_2 but leads to non-cryst. products. Hydrolysis of (V) by aq. $\text{Na}_2\text{B}_4\text{O}_7$,

gives a substance very similar to but not identical with methylreductive acid (*loc. cit.*) and isoanhydrocalotropagenin, $\text{C}_{23}\text{H}_{32}\text{O}_6$, decomp. 251° after softening at 247°, obtained previously (*loc. cit.*) from (I). (V) and (I) are therefore derived from the same fundamental substance. (III), decomp. 244°, $[\alpha]_D + 74^\circ \pm 4^\circ$ in CHCl_3 , is $\text{C}_{29}\text{H}_{40}\text{O}_{10}$ (also $+1\text{H}_2\text{O}$ and $+1\text{EtOH}$); it is therefore a hydroxycalotropin. Physiologically it resembles strophanthin-g. Like (I) and (II) it is very resistant towards acids and only in presence of $(\text{NO}_2)_2\text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{NH}_2$ or other osazone-formers are dil. acids effective. It is rapidly hydrolysed by alkali to *anhydrocalotropagenin*, decomp. 241°, obtained previously from (I). (I) and (III) are therefore derived from the same fundamental substance. The mother-liquors from the hydrolysis give the *phenylosazone*, decomp. 151—152°, of a substance, $\text{C}_6\text{H}_8\text{O}_4$, and with 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{NH}_2$ the derivative, $\text{C}_{18}\text{H}_{14}\text{O}_9\text{N}_8$, decomp. 214—217°, of an anhydro-compound, $\text{C}_6\text{H}_6\text{O}_3$. Thermal decomp. of (III) gives the compound, $\text{C}_6\text{H}_8\text{O}_4$, which shows the strong reducing action of enediols towards neutral AgNO_3 , 1, and FeCl_3 ; it is probably a hydroxymethylreductive acid. (IV) is not invariably found in the sap and appears to be more abundantly present as the content of (II) diminishes. It is possible that it is an after-formation due to some fermentative process. It is very similar to (I), giving on hydrolysis methylreductive acid with a genin which is not identical with calotropagenin. The pure poisons show marked differences in the ultra-violet fluorescence colours when the Liebermann reaction is effected with H_3PO_4 instead of H_2SO_4 or when in the Kiliani reaction FeCl_3 is replaced by MnCl_2 or SbCl_5 . The reactions are very sensitive to impurities and hence unsuitable for crude fractions. (II) can be detected by alkali plumbite but the change is not very sensitive. Janus-red is decolorised in warm solution in a short time by *Calotropis* poisons but not by normal glucosides (antiarr gives 50% decolorisation). Most *Calotropis* poisons with 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{NH}_2 \cdot \text{HCl}$ give an orange-red ppt. within a few hr.; this dissolves in alcoholic alkali to an intensely blue or violet-blue solution whereas other glucosides give only a blood-red to yellow colour and, frequently, no ppt. H. W.

Melanoidins and their relation to humic acids.

C. ENDERS and K. THEIS (Brennstoff-Chem., 1938, 19, 360—365, 402—407, 439—449).—Melanoidin (I), prepared by heating glucose with glycine in aq. solution, was sol. in aq. alkali, slightly sol. in H_2O , and insol. in org. solvents. The kinetics of formation was studied, the (I) being determined colorimetrically; the rate of formation increased with rising temp. and increasing p_H . The composition and mol. wt. of the (I) corresponded with $\text{C}_{67}\text{H}_{76}\text{O}_{32}\text{N}_5$; the mol. contained 8 alcoholic and 3 phenolic OH, 3 CO, and 5 CO_2H . In properties and reactions (I) closely resembled Merck's humic acid. At 150° it "coalified" with the loss principally of CO_2 and H_2O and with decreasing solubility in aq. alkali. During coalification the N at first increased but passed through a max. and then decreased; the CO decreased whilst the phenolic OH remained const. The changes are

similar to those that occur on heating humic acid except that they occur somewhat more readily and can be correlated with the natural coalification series humic acid-brown coal-bituminous coal-anthracite. Oxidation of (I) led through the formation of some unidentified intermediate products (one of which, $C_5H_{12}O_2N_4$, had m.p. 156°) to oxalic, glycollic, succinic, and picric acids, and a dihydroxybenzenedicarboxylic acid. A. B. M.

Chemistry of *Aspergillus* colouring matters.

II. J. H. CRUICKSHANK, H. RAISTRICK, and R. ROBINSON (J.C.S., 1938, 2056—2064).—Auroglaucon (I) forms $(K_2CO_3 \cdot MeI)$ a *Me ether*, m.p. 100° [oxime, m.p. 117° (decomp.)], which shows a Fe^{+++} reaction; a Me_2 ether could not be obtained. Flavoglaucon (II) is reduced (Pd-H₂) to dihydroflavoglaucon (III), m.p. 98° (2:4-dinitrophenylhydrazine, m.p. 203°), which condenses with $o\text{-}C_6H_4(NH_2)_2$ to a substance, m.p. 150° , and is oxidised ($KMnO_4$) to *n*-octoic acid. Reduction (Pd-H₂) of the *Me ether* of (I) gives dihydroflavoglaucon *Me ether* (2:4-dinitrophenylhydrazine, m.p. 193°), which is oxidised ($NaOH\text{-}H_2O_2$) to *n*-octoic acid. Further reduction of (I) affords decahydroauroglaucon (tetrahydroflavoglaucon), m.p. 85° , which forms a Ac_2 derivative, m.p. 70° , and a Me_2 ether, m.p. 79° . $Zn\text{-}AcOH$ with (III) yields tetrahydrodeoxyflavoglaucon (Me_2 ether, b.p. $175\text{--}180^\circ/0.02$ mm.). Comparative diazo-coupling and bromination tests of (I) and (II) and their derivatives with synthetic substances indicate resemblance to 4-*n*-amylquinooctophenone. These results confirm and extend the deductions arrived at for the structure of (I) and (II) (A., 1937, II, 106); (II) is regarded as an *n*-octoylisopentenylquinol or an *n*-octoylvinylisopropylquinol and (I) has the same skeleton with three more double linkings. 3:6-(OMe)₂ $C_6H_2(CO)_2O$, $o\text{-}C_6H_5Me \cdot OMe$, and $AlCl_3$ give 3:6:6'-trimethoxy-2-methylbenzoic acid, m.p. 218° , which with H_2SO_4 yields 5:8-dihydroxy-3-methoxy-2-methylanthraquinone, m.p. $194\text{--}195^\circ$, methylated to the 3:5:8-(OMe)₃ compound, m.p. 231° . This substance is demethylated to the 3:5:8-(OH)₃-derivative (+0.6 H_2O), m.p. 254° (Ac_3 derivative, m.p. 196°). F. R. S.

Synthesis of substances with morphine-like action. H. HENECKA (Med. u. Chem., 1936, 3, 403—407; Chem. Zentr., 1937, i, 1146—1147).— $NEt_2 \cdot [CH_2]_3 \cdot COMe$ (I), C_2H_5 , and $NaNH_2$ in Et_2O give α -diethylamino- δ -hydroxy- δ -methyl- Δ^6 -hexenene, b.p. $84\text{--}85^\circ/3$ mm., the Na salt (II) of which with $COMe_2 + NaNH_2$ affords α -diethylamino- δ - γ -dihydroxy- δ - γ -methyl- Δ^6 -octenene, b.p. $126^\circ/1$ mm. This is converted ($HgSO_4$ in 10% H_2SO_4 at $80^\circ/48$ hr.) into 4(or 3)-keto-2:5:5-trimethyl-2- γ -diethylaminopropyl-tetrahydrofuran, b.p. $110\text{--}111^\circ/4$ mm., reduced (Na , $EtOH$) to the 4(or 3)- OH -derivative, b.p. $126\text{--}128^\circ/3$ mm. $\alpha\kappa$ -Bisdiethylamino- δ - γ -dihydroxy- δ - γ -methyl- Δ^6 -decenene, b.p. $175\text{--}180^\circ/1$ mm.: [from (I), (II), and $NaNH_2$ in Et_2O], similarly gives 3-keto-2:5-dimethyl-2:5-bis- γ -diethylaminopropyltetrahydrofuran, b.p. $162\text{--}164^\circ/2.5$ mm., and thence the 3- OH -derivative, b.p. $165\text{--}168^\circ/1$ mm. The furans have no morphine-like action. H. B.

Constitution of usnic acid. C. SCHÖPF and F. ROSS (Naturwiss., 1938, 26, 772—773; cf. A., 1937,

II, 347; 1938, II, 198; 1939, II, 32).—Usnic acid diacetate (I) with O_3 in CCl_4 affords an ozonide (II), $C_{22}H_{20}O_{12}$, decomp. 152° , catalytic hydrogenation of which removes 1 H_2O to give a non-cryst. product. When heated with $EtOH$ (II) affords *Et* α -diketovalerate and 1-keto-3:5-diacetoxy-6-acetyl-2:4-dimethyl-1:2-dihydrobenzofuran (III), m.p. 132° , which gives no $FeCl_3$ reaction, but contains the methylphloroglucinol ring and both Ac groups of (I). With conc. H_2SO_4 or $HCl\text{-}EtOH$, (III) affords a substance, $C_{12}H_{12}O_5$, m.p. 223° after sintering at 195° , re-acetylated to an isomeride, m.p. 132° , of (III). *d*-Diacetoxy-usnic acid with O_3 gives, in solution, a strongly dextrorotatory ozonide which when decomposed affords (III). J. L. D.

Syntheses of chroman derivatives with the ring system of α -tocopherol. I. W. JOHN, P. GÜNTHER, and M. SCHMEL (Ber., 1938, 71, [B], 2637—2649).—Gradual addition of trimethylquinol (I) and $CH_2Ac \cdot CO_2Me$ in $MeOH$ to P_2O_5 at 0° and heating of the mixture to $120\text{--}140^\circ$ gives 6-hydroxy-2:3:5:7:8-pentamethylchromone, m.p. 201° , hydrogenated (Pd sponge in $AcOH$) to 6-hydroxy-2:3:5:7:8-pentamethylchroman, m.p. 108° . Analogously, $CH_2Ac \cdot CO_2Et$ affords 6-hydroxy-2:3:5:7:8-tetramethyl-chromone and -chroman, m.p. 145° [allophanate, m.p. about 220° (decomp.)]. With $COPr^+ \cdot CH_2 \cdot CO_2Et$ a compound, $C_{17}H_{22}O_5$, m.p. 141° , results, hydrogenated to a substance, $C_{17}H_{26}O_5$, m.p. 112° , which is not a chroman derivative. P_2O_5 and (I) do not appear to react with *Me* α -cetylacetoacetate, b.p. $170^\circ/0.25$ mm., m.p. $36\text{--}37^\circ$, obtained from $CH_2Ac \cdot CO_2Me$, cetyl bromide, and $NaOMe$ in $MeOH$. (I) is converted by dimethylacrylyl chloride and $AlCl_3$ in $PhNO_2$ at $75\text{--}80^\circ$ into 6-hydroxy-2:2:5:7:8-pentamethylchromanone (II), m.p. 162° ; in CS_2 the reaction follows a different course, giving a compound (III), $C_{14}H_{18}O_3$, m.p. 109° , isomeric with (II) but not containing an aromatic system and a substance (IV), $C_{14}H_{18}O_3$, m.p. 117° , possibly a dihydrocoumarin derivative. In $PhNO_2$ at room temp. (III) and (IV) are obtained. (II) is reduced (Clemmensen) to 6-hydroxy-2:2:5:7:8-pentamethylchroman (V), m.p. $93\text{--}94^\circ$ (allophanate, m.p. 230°). The most successful syntheses in the series are effected by Grignard's reagents. Thus, 6-hydroxy-5:7:8-trimethyl-3:4-dihydrocoumarin (VI) is transformed by $MgMeI$ into (V) (*p*-bromobenzoate, m.p. 159°). Similarly (VI) and (VII) in $Et_2O\text{-}C_6H_5\text{-}PhOMe$ yield 6-hydroxy-5:7:8-trimethyl-2:2-didodecylchroman, m.p. about 28° (allophanate, m.p. 116°). 6-Hydroxy-2:5:7:8-tetramethyl-2-dodecylchroman, m.p. $60\text{--}61^\circ$ (allophanate, m.p. 180°), is obtained by the simultaneous action of $MgMeI$ and (VII) on (VI). Dodecyl allophanate, m.p. 150° , and dodecylurethane, m.p. 84° , are described incidentally. H. W.

Synthesis of chromones. F. VON WERDER and F. JUNG (Ber., 1938, 71, [B], 2650—2652).—Trimethylquinol, $CH_2Ac \cdot CO_2Et$, and P_2O_5 in $EtOH$ at 140° give 6-hydroxy-2:5:7:8-tetramethylchromone (I), m.p. 224° , converted by boiling Ac_2O into its acetate (II), m.p. 172° . Trimethylquinol diacetate is transformed by $AlCl_3$ at 220° into (II), (I) (possibly formed during the working up of the product), and 2:5-dihydroxy-

3 : 4 : 6-trimethylacetophenone, m.p. 152° (monoacetate, m.p. 113°), which does not react with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, NH_2OH , or $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, but is reduced (Clemmensen) to 3 : 6-dihydroxy-1 : 2 : 4-trimethyl-5-ethylbenzene, m.p. 165°. H. W.

Aminobenzylidenechromanones. P. PFEIFFER and G. VON BANK (J. pr. Chem., 1938, [ii], 151, 319—326).—Addition of $\text{NaOMe}\cdot\text{MeOH}$ to 7-methoxychromanone (I) and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ gives 7-methoxy-3-m-nitrobenzylidenechromanone, m.p. 147—148°, reduced (SnCl_2 and HCl in AcOH) to 7-methoxy-3-m-aminobenzylidenechromanone, m.p. 106° (hydrochloride, m.p. (indef.) 230°; Bz derivative, m.p. 165°), which, in conc. H_2SO_4 , gives a colourless solution with very pale, blue-green fluorescence. Similarly, 7-hydroxychromanone affords 7-hydroxy-3-m-nitrobenzylidenechromanone, m.p. 242.5° after becoming brown at 230° (acetate, m.p. 138.5°), whence 7-hydroxy-3-m-aminobenzylidenechromanone, m.p. 241.5° after softening at 238° (hydrochloride, m.p. 185°, decomp. 205°). $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (I) yield 7-methoxy-3-p-nitrobenzylidenechromanone, m.p. 174—175° after softening at 170°. $p\text{-NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (I) in EtOH saturated with HCl at 0° give 7-methoxy-3-p-benzamidobenzylidenechromanone, m.p. 209° (slight decomp.). 7-Hydroxy-3-p-nitro-, m.p. 211° (decomp.) (acetate, m.p. 207—208°), and 7-hydroxy-3-p-benzamido- (acetate, m.p. 205°) -benzylidenechromanone are described. H. W.

Magnetochemical investigation of organic compounds. XV. Constitution and magnetic behaviour of metallic ketyls. E. MÜLLER and W. WIESEMANN (Annalen, 1938, 537, 86—112).—The metal compounds are divided into actual radicals, "holoradicals," meriradical, and non-radical substances. Previously reported, non-radical compounds all belong to the 4-pyrone series. In extension it is shown that the K compounds of chromone and 2-phenylchromone are diamagnetic. The former contains 2 CO per K whereas all other compounds have $\text{CO} : \text{K} = 1 : 1$. There is therefore no relationship between radical structure and K content per CO. The constitution of the non-radicals is investigated with Li methylchromone (I), which is readily obtained from LiBu and methylchromone (II). It is diamagnetic. With BzBr , Br , or MeI it gives resins from which a cryst. material cannot be isolated. Hydrogenation ($\text{Pd}\cdot\text{CaCO}_3$ in C_6H_6) of (I) and hydrolytic removal of Li leads to a non-cryst. mixture of 2-methylchromanone (III) and 2-methylchromanol (IV). [Hydrogenation ($\text{Pd}\cdot\text{CaCO}_3\cdot\text{C}_6\text{H}_6$) of 2-methylchromone gives (III) ($p\text{-nitrophenylhydrazone}$, m.p. 253°), further hydrogenated (Pt-black in C_6H_6) to (IV) (benzoate, m.p. 70°).] (I) must therefore be formulated either as a quinhydrone or as a pinacolate; the latter is preferred since the production of (II) cannot be observed when (I) is cautiously decomposed with dil. acids. An electronic structure is also discussed. The meriradical compounds formed by addition of alkali metals to non-enolisable ketones are to be regarded as mol. compounds of complex structure. Their common characteristic is that one atom of metal is invariably added for 2 CO of the initial ketone. The alkali metal compounds so produced are

mol. compounds of the radical-quinhydrone or pinaconate-quinhydrone the composition of which depends on the temp. Investigations with K benzil or K phenanthraquinone show that with spatially proximate CO groups the second CO which does not add metal can function as an internal quinhydrone. In the case of K p -dibenzoylbenzene a pinaconate-quinhydrone is not formed but a diamagnetic "quinonoid" dimetallic compound results. Peculiarities in the constitution of the initial ketone are therefore operative. Since paramagnetism decreases with decreasing temp. there is a displacement towards the non-radical form even in the solid state. The magnitude of this displacement over the range, room temp. to liquid air, depends on the constitution of the initial material. The radical condition of most of these meriradical substances can be stabilised only when the lone electron can be merged into a large cloud of π electrons. If the electron cloud of the unimol. compound is inadequate, as in these cases, further mols. are brought in. Thus two xanthone mols. add 1 K atom and hence a π electron in common. At low temp. there is partial compensation between two vicinal adducts. The holoradical compound from K and $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}$ contains 77—74% of radical; the content sinks to about 60% of the solution is cooled from room temp. to that of liquid air. The effect appears general. H. W.

Chalkones. Synthesis of 1-p-alkoxyarylidene-5 : 6-benzocoumaran-2-ones. A. P. KHANOLKAR and T. S. WHEELER (J.C.S., 1938, 2118—2119).—1-Hydroxy-2-naphthyl p -alkoxystyryl ketone dibromides, which normally yield flavones with alcoholic alkali, give β -alkoxy-compounds and then arylidene-coumaranones, if the solubility of the dibromide in alcohols is increased by addition of CHCl_3 . With aq. alkali and COMe_2 the dibromides give the corresponding naphthaflavones. The following are described : 4-bromo-1-hydroxy-2-naphthyl $\alpha\beta$ -dibromo-, m.p. 173°, α -bromo- β -ethoxy-, m.p. 169—171°, and α -bromo- β -methoxy- β -3 : 4-methylenedioxyphenylethyl ketone, m.p. 169—170°; 6-bromo-3' : 4'-methylenedioxy- α -naphthaflavone, m.p. 276°; 4-bromo-1-hydroxy-2-naphthyl $\alpha\beta$ -dibromo-, m.p. 157—158°, α -bromo- β -ethoxy-, m.p. 155—156°, and α -bromo- β -methoxy- β - p -anisylethyl ketone, m.p. 146—147°; 4-bromo-1-hydroxy-2-naphthyl p -methoxystyryl ketone, m.p. 184°; 6-bromo-4'-methoxy- α -naphthaflavone, m.p. 240—241°; and 4-bromo-1-anisylidene-5 : 6-benzocoumaran-2-one, m.p. 219—220°. F. R. S.

Pyrilium salts from acid anhydrides and acid chlorides. P. P. HOFF and R. J. W. LE FÈVRE (J.C.S., 1938, 1989—1991).—By the interaction of COPhMe (2 mols.) or dypnone with various acid anhydrides or chlorides (1 mol.), in the presence of FeCl_3 , a no. of 2-substituted 4 : 6-diphenylpyrilium ferrichlorides have been prepared. No marked condensation occurs in the absence of FeCl_3 , and the effective intermediates may be of the type $\text{RCOCl} + \text{FeCl}_3$. The following are new : 4 : 6-diphenyl-2-ethyl-, m.p. 166°, - n -propyl-, m.p. 198°, -isopropyl-, m.p. 258°, -isobutyl-, m.p. 162°, - n -amyl-, m.p. 144°, -hexyl-, m.p. 88°, -styryl-, m.p. 257°, and -benzylpyrilium ferrichloride, m.p. 203°. F. R. S.

Melting point of psoralen (ficusin). K. OKAHARA (Bull. Chem. Soc. Japan, 1938, 13, 653—655; cf. A., 1936, 861, 1121; 1937, II, 112).—Carefully purified natural psoralen and the synthetic product (method of Späth *et al.*) both melt at 161—162°.

A. LI.

Preparation and properties of pure dioxan. K. HESS and H. FRAHM (Ber., 1938, 71, [B], 2627—2636).—The changes which occur in dioxan (I) when kept are due to union with atm. O₂ to form a peroxide; the change is accelerated by impurities and by the consequential products. In absence of air pure (I) can be kept unchanged at will. It may be advisable to remove ethylene acetal, $\begin{smallmatrix} \text{CH}_2\text{O} \\ \text{CH}_2\text{O} \end{smallmatrix} > \text{CHMo}$, from crude (I) by boiling with 10% of N-HCl but if it is present only in small amount, a prolonged heating with Na is adequate. Subsequent operations included careful fractionation and repeated freezing, which require the complete absence of atm. moisture. The physical methods used in controlling the purity of (I) are constancy of m.p. when fractionally frozen, equality of the temp. of boiling and condensation, and equality of the vapour tension of the liquid itself and of that produced by condensing its vapour. Peroxide is detected by Rieche's benzidine reaction or by the (very sensitive) conversion of Hg into black Hg₂O. Aldehyde is detected by Schiff's reagent. Pure (I) has m.p. 11·80° ± 0·01° (corr.), b.p. 101·31° (corr.)/760 mm., d_{20}^{20} 1·03375 ± 1 × 10⁻⁵ g./c.c., n_D^{20} 1·42241 ± 1 × 10⁻⁵. At room temp. pure (I) has very little action on O₂ so that it can be kept in contact with air but a comparatively rapid change occurs at the b.p. It appears that the changes occur in the sequence: (I) → oxonium peroxide → aldehyde → peroxide.

H. W.

Synthesis of β-2-thienylalanine and of β-2-thienylethylamine. G. BARGER and A. P. T. EASSON (J.C.S., 1938, 2100—2104).—Thiophen (improved prep. from C₆H₂ and FeS₂) is converted, through 2-thienyl Me ketone and 2-thienylglyoxylic acid, into thiophen-2-aldehyde. This with hippuric acid gives the *azlactone* of α-benzamido-β-2-thienylacrylic acid, m.p. 175°, the free acid, m.p. 238—240°, from which is reduced (Na-Hg) to the *propionic acid*, m.p. 176—180°, hydrolysed to β-2-thienylalanine, m.p. 274—275°. This compound is more readily prepared from the aldehyde with hydantoin through *acetyl-2-thienylidenhydantoin*, m.p. 214—216°, *2-thienylidenhydantoin*, m.p. 253—255°, and *2-thienylmethylhydantoin*, m.p. 188—190°. β-2-Thienylpropionamide, m.p. 99—100°, obtained from the corresponding acid, with Cl₂-KOH gives β-2-thienylethylamine, b.p. 200—201°/750 mm. (*hydrochloride*, m.p. 200—202°). This amine has a pressor action qualitatively and quantitatively indistinguishable from that of Ph·[CH₂]₂·NH₂, a finding attributed to the similarity in physical properties of the two bases. Oximinoacetothienone is reduced (SnCl₂) to 2-thienylaminomethyl ketone *hydrochloride*, m.p. 215—218°.

F. R. S.

Highly arylated compounds. VIII. Derivatives of tetraphenylthiophen. W. DILTHEY and E. GRAEF (J. pr. Chem., 1938, [ii], 151, 257—278).—Gradual addition of rather > the calc. amount of

conc. H₂SO₄ to tetraphenylthiophen (I) and the calc. amount of KNO₃ in AcOH at 100° affords 3:4:5-triphenyl-2-p-nitrophenylthiophen (II), m.p. 179—180°, in 60% yield. It gives p-NO₂·C₆H₄·CO₂H when oxidised. Reduction (SnCl₂-HCl-AcOH) of (II) gives 3:4:5-triphenyl-2-p-aminophenylthiophen, m.p. 204—205° (Ac derivative, m.p. 258°; corresponding *diazonium perchlorate*; *anisylidene* derivative, m.p. 201°). (II) is oxidised by H₂O₂ to the corresponding *sulphone*, m.p. 250°, which gives an intense violet-red halochromism with NaOMe in C₆H₅N and affords only BzOH and p-NO₂·C₆H₄·CO₂H when degraded with O₃. Gradual addition of conc. HNO₃-AcOH to (I) suspended in AcOH at 100° leads to 3:4-diphenyl-2:5-di-p-nitrophenylthiophen (III), m.p. 217—218°, with a smaller proportion of 4:5-diphenyl-2:3-di-p-nitrophenylthiophen (IV), m.p. 169—170°, either of which gives exclusively p-NO₂·C₆H₄·CO₂H when oxidised. (III) is reduced (SnCl₂-HCl-AcOH) to 3:4-diphenyl-2:5-di-p-aminophenylthiophen, m.p. 273° [Ac, m.p. 324—325°, Bz, m.p. 320°, and *dianisylidene*, m.p. 243°, derivatives; *compound*, C₄₈H₃₂O₂N₄S, m.p. 267°, obtained by coupling diazotised (III) with 2-C₁₀H₇-OH]. Oxidation of (III) by H₂O₂ in AcOH or sulphoacetic acid affords the corresponding *sulphone* (V), m.p. 294°, oxidised by H₂O₂, O₃, or CrO₃ exclusively to p-NO₂·C₆H₄·CO₂H; it appears to add 1 NaOMe. (IV) is reduced to 4:5-diphenyl-2:3-di-p-aminophenylthiophen, m.p. 220°, which gives a weak yellow-orange halochromism in conc. H₂SO₄, and is oxidised by H₂O₂ to 4:5-diphenyl-2:3-di-p-nitrophenylthiophen dioxide (VI), m.p. 194°, which shows a violet-red halochromism with NaOMe in C₆H₅N. Fuming HNO₃ at >0° transforms (I) into *hexanitrotetraphenylthiophen*, m.p. 284°, probably identical with the (NO₂)₄-derivative described by Fleischer. Nitration of (II) gives a mixture of (III) and (IV). Nitration of (III) by fuming HNO₃ in AcOH at 100° gives *tetranitrotetraphenylthiophen*, m.p. 302°, in small amount; the main product appears to be a mixture of several NO₂-compounds. *pp'*-Dinitrodibenzyl sulphide is oxidised by H₂O₂ to *pp'*-dinitrodibenzyl sulphone, m.p. 259°, the colour reactions of which closely resemble those of (V) and (VI). The choice of formulæ for (III) and (IV) is dictated by this consideration, by analogies of m.p., and by the isolation of small amounts of benzil by the oxidation of (IV).

H. W.

Attempted preparation of an optically active 4:4'-dithioxanthyl. W. STEINKOPF and L. GARBE (J. pr. Chem., 1938, [ii], 151, 327—330).—2:2'-Diiododiphenyl, o-SH·C₆H₄·CO₂H, anhyd. K₂CO₃, and Cu(OAc)₂ in anhyd alcohol under CO₂ at 220° give 2:2'-di-o-carboxyphenylthioldiphenyl (I), m.p. 254°. This gives two *quinine* salts, C₂₆H₁₈O₄S₂·C₂₀H₂₄O₂N₂, m.p. 228° and 222°, respectively, from which the optically active *acids*, m.p. 259°, [α]_D²⁵ +194·3° in abs. EtOH, and m.p. 265°, [α]_D²⁵ -62·3° in abs. EtOH, are isolated. Conc. H₂SO₄ at 90° transforms (I) into (?) 4:4'-dithioxanthyl, which becomes dark brown without melting at 350°; the solubility of the analogous product obtained from the optically active *acids* is so small that possible optical activity could not be investigated.

H. W.

Extension of Knorr's pyrrole synthesis. D. DAVIDSON (J. Org. Chem., 1938, 3, 361—364).—Amarone and Zn dust in AcOH give tetraphenylpyrrole (I) (cf. A., 1938, II, 114). With $\text{COPh}\cdot\text{CH}_2\text{Ph}$ and NH_4OAc , $\text{COPh}\cdot\text{CHPh}\cdot\text{NH}_2$ or benzoin gives 74% of (I); in absence of NH_4OAc , $\text{COPh}\cdot\text{CHPh}\cdot\text{NH}_2$ gives only 33% of (I). 50% of (I) is also obtained from benzoin, NH_4OAc , and Zn dust (to produce $\text{COPh}\cdot\text{CH}_2\text{Ph}$) in AcOH. With benzoin and NH_4OAc in AcOH, $\text{COMe}\cdot\text{CH}_2\text{Ph}$, $\text{CO}(\text{CH}_2\text{Ph})_2$, and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ give 3:4:5-triphenyl-2-methyl-, m.p. 164° (corr.), and -2-benzyl-pyrrole, m.p. 151° (corr.), and Et 4:5-diphenyl-2-methylpyrrole-3-carboxylate, m.p. 203° (corr.), but COPhMe does not react.

R. S. C.

Oxidation products of pyrrole amines. II. T. AJELLO and G. SIGILLÒ (Gazzetta, 1938, 68, 681—688).—The substance, m.p. 170°, obtained from 4-amino-2:3:5-triphenylpyrrole and $\text{K}_3\text{Fe}(\text{CN})_6$ or PbO_2 (cf. A., 1939, II, 35) is identified (mol. wt.) as 4-imino-2:3:5-triphenylpyrrole, which is converted by dil. AcOH into triphenylpyrrolylhydroxylamine and the substance of m.p. 290° (*loc. cit.*), and by dil. HCl or H_2SO_4 in aq. EtOH into a substance, m.p. 188°.

E. W. W.

Pyridine-N-oxide-O-sulphonic acid betaine.—See A., 1939, I, 91.

Condensation products of (A) acetylisatic acid, (B) isatin. M. YOKOYAMA (J. Chem. Soc. Japan, 1936, 57, 247—250, 251—254).—(A) Acetylisatic acid [(?) quinoline salt (I), m.p. 177.5°, decomposes when kept in EtOH giving isatin, quinoline, and AcOH] with hydantoin and AcOH-NaOAc at 107° affords acetyloxindolylidenhydantoin (II), m.p. 290° (decomp.), similarly prepared from (I) in presence of saturated aq. NaCl at 105—110°. Hydrolysis (aq. NH_3) of (II) gives oxindolylidenhydantoin, m.p. >310°, reduced (Na-Hg, dil. NaOH) to oxindolylhydantoin (+ H_2O), m.p. 204—205°, which is hydrolysed [$\text{Ba}(\text{OH})_2$] to NH_3 and 2:3-dihydroxy-3:4-dihydroquinoline-4-carboxylic acid, m.p. >300° (Ag salt when slowly heated gives a sublimate of 2-hydroxyquinoline).

(B) Isatin (1 mol.) with 1 and 2 mols. of $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in EtOH-piperidine gives Et oxindolylidenecyanoacetate (III), m.p. 202°, and Et₂ indole-2:3-dicyanoacetate (+ H_2O), m.p. 99—100°, respectively. EtOH-conc. H_2SO_4 converts (III) into Et H (IV), m.p. 219°, and Et₂, m.p. 149°, oxindolylidenemalonate. Dissolution of (IV) in alkali and acidification gives 2-hydroxyquinoline-3:4-dicarboxylic acid, m.p. 304—305° [3-Et₂ ester, m.p. >305°, obtained by reduction (Al-Hg, alkali) of (III) and treatment of the product with EtOH-conc. H_2SO_4]. Reduction (SnCl_2 , AcOH) of (III) affords β-amino-α-oxindolylpropionic acid, m.p. 94°. CH. ABS. (b)

Hypaphorine: racemisation of its ester and properties of other derivatives. W. M. CAHILL and R. W. JACKSON (J. Biol. Chem., 1938, 126, 627—631; cf. J.C.S., 1911, 99, 2068).—Hypaphorine Me ester iodide (I) is completely racemised when heated with MeOH-MeI-NaOH for 8 hr., and is hydrolysed by aq. NaOH to a partly racemised betaine. dl-Hypaphorine melts at 248—249° (decomp.). Hypa-

phorine gives with HNO_3 the nitrate, $[\alpha]_D^{25} +91.2^\circ$ in aq. NH_3 , and with HI the iodide, m.p. 220—221° (decomp.), $[\alpha]_D^{25} +75.2^\circ$ in aq. NH_3 [produced together with the nitrate by hydrolysing (I) and adding HNO_3]. All m.p. are corr. A. LI.

Direct introduction of the amino-group into the aromatic and heterocyclic nucleus. IV. Action of the alkali and alkaline-earth amides on some substituted quinolines. F. W. BERGSTROM (J. Org. Chem., 1938, 3, 233—242; cf. A., 1938, II, 245).—Introduction of NH_2 by $\text{Ba}(\text{NH}_2)_2$, or sometimes KNH_2 or $\text{KNH}_2\cdot\text{Ba}(\text{CNS})_2$, in liquid NH_3 gives (? 2-)amino-8-, m.p. 86—86.3° (picrate, m.p. 242—243.5°), and -6-methyl-, m.p. 145.7—146.7°, -6-, m.p. 178.7—179.4°, and -8-ethoxy-, m.p. 211—212°, -6-dimethylamino-, m.p. 168.5—169.5°, -quinoline, 4-aminoquinoline-2-, (?) +0.25 H_2O , m.p. 280.5—281° (decomp.), and 2-aminoquinoline-4-sulphonic acid (I), m.p. (crude) 350—352° (Et ester, m.p. 191—192°), (?) 2-)aminoquinoline-6-carboxylic acid, +0.5 H_2O , m.p. 323—324°, and aminoquinoline-6-sulphonic acid, + H_2O , m.p. >354°. No NH_2 -derivative could be obtained from 7-methyl-, 2-methoxy- [gives 2-aminoquinoline (II)], 8- or 2-hydroxy-quinoline (II), or quinoline-2-sulphonic acid (III). KNH_2 usually gives tars; with 6-methoxyquinoline it gives products (? the 2- and 4- NH_2 -compounds), m.p. 119—121.5° and 160—175°, and with (III) gives (II) and a product, $\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_3$, m.p. 209—210° [or, in presence of KNO_3 , (II)]. With $\text{KNH}_2\cdot\text{Ba}(\text{CNS})_2$ quinoline-4-carboxylic acid gives a poor yield of (I) or a substance, $\text{C}_{10}\text{H}_9\text{ON}_3$, m.p. 211.4—212.4°. CO_2H at $\text{C}_{(2)}$ or $\text{C}_{(4)}$ increases the yield of NH_2 -derivative. R. S. C.

Aminoquinolines.—See B., 1939, 18.

Application of the Bischler-Napieralski reaction to δ-ketoazelaodi-β-veratrylethylamide. F. E. KING and R. ROBINSON (J.C.S., 1938, 2119—2120; cf. Child and Pyman, A., 1929, 1314).—Me δ-ketoazelaate (I), new m.p. 34°, boiled with dil. HCl for 5 min. and the solution evaporated at 60°/vac., gives δ-ketoazelaic acid, m.p. 108—109°. (I) and 2 equivs. of β-veratrylethylamine at 170—180° afford δ-ketoazelaodi-β-veratrylethylamide, m.p. 147° (2:4-dinitrophenylhydrazones, m.p. 135—136°), converted by $\text{POCl}_3\cdot\text{PhMe}$ at 110° into γγ'-bis-(6:7-dimethoxy-3:4-dihydroisoquinolyl)dipropyl ketone [monopicrate, m.p. 181—182°, accompanied by a little of a picrate, m.p. 112—113° (decomp.)]. A. T. P.

Formation of isocyanine dyes by intermolecular condensation of 4-chloroquinolines. A. MEYER and H. DRUTEL (Compt. rend., 1938, 207, 923—925).—When 4-chloro-2:6-dimethylquinoline (I) (cf. A., 1937, II, 431) containing a little impurity or H_2O is heated, an isocyanine dye (II) is formed. (I) forms a quaternary NH_4 chloride which loses HCl to give 4-keto-2:6-dimethyl-1:4-dihydroquinoline, two mols. of which condense to give (II). A dry C_6H_6 solution of the product left when (II) is washed with NaOH ppts., with Et_2O , a rose-coloured dye (III), $\text{C}_{22}\text{H}_{18}\text{ON}_2$, which with dry HCl (gas) in C_6H_6 forms a hydrochloride, $\text{C}_{22}\text{H}_{19}\text{ON}_2\text{Cl}$, m.p. >300°, of isocyanine-blue, which with NaOH becomes Cl-free. 4-

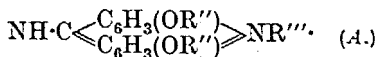
Chloro-2 : 8-dimethylquinoline does not give an isocyanine.
J. L. D.

Carbazole ketones.—See B., 1939, 18.

Phthaloyl- and dibenz-carbazoles.—See B., 1939, 21.

2 : 8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the 5-carbon atom. XVII. Synthesis of 5-*o*-amino-anilino-2 : 8-dialkoxy-10-alkylacridinium derivatives and 5 : 5'-*o*-phenylenebis(amino-2 : 8-dimethoxy-10-methylacridinium hydroxide). XVIII. Synthesis of the hydrochlorides of 5-*m*-amino-anilino-2 : 8-dialkoxy-10-alkylacridinium chlorides and 5 : 5'-phenylenediamino-compounds combined with various kinds of acridinium derivatives. XIX. Relation between 2 : 8-dialkoxy-*N*-alkylacridones and solvents. K. ISHIIHARA (J. Chem. Soc. Japan, 1936, 57, 12—25, 136—165, 326—345; cf. A., 1937, II, 468).—XVII. 5-Chloro- (or iodo)-2 : 8-dialkoxy-10-alkylacridinium chlorides (or iodides) and *o*-C₆H₄(NH₂)₂ give the 5-*o*-aminoanilino-derivatives solely. 5-*o*-Aminoanilino-2 : 8-dimethoxy-10-methyl-, m.p. 250° (decomp.), and -ethyl-, m.p. 231°, -acridinium iodide, and the -2 : 8-diethoxy-10-methyl chloride, m.p. 248° (decomp.), and iodide, m.p. 238°, and -10-ethyl chloride, m.p. 245° (decomp.), and iodide, m.p. 245°, are prepared. 5-*o*-Aminoanilino-2 : 8-dimethoxy-10-methylacridinium hydroxide is converted by 70% MeOH or C₆H₆-H₂O at 100°/10—15 hr. (sealed tube) into 2 : 8-dimethoxy-*N*-methylacridone (28%) and 5 : 5'-*o*-phenylenebis(amino-2 : 8-dimethoxy-10-methylacridinium hydroxide) (24—28%).

XVIII. 5-*m*-Aminoanilino-2 : 8-dialkoxy-10-alkylacridinium hydroxides and ± 2 mols. of HCl in aq. AcOH give the *acridinium chloride hydrochlorides* (contain 0.9HCl); the 2 : 8-dimethoxy-10-methyl (+1½H₂O, ½AcOH), m.p. 215° (decomp.), and -ethyl (+1½H₂O, ½AcOH), m.p. 206° (decomp.), and 2 : 8-diethoxy-10-methyl (+1H₂O), m.p. 248° (decomp.), and -ethyl (+1½H₂O), m.p. 240° (decomp.), derivatives are prepared. When these (singly or mixtures of two) are heated at 75°/2 hr. and the products treated with boiling aq. AcOH-KI, the basic *iodides*, Al₂.xAl(OH).yH₂O.zAcOH, are obtained; these with aq. KOH give the *hydroxides*, A(OH)₂. The respective m.p. of the iodides and hydroxides (for R, R', R'', R''' in the order quoted) are : Me, Me, Me, Me, 284°,

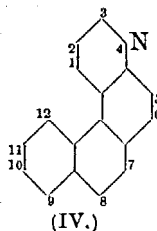


—; Et, Me, Me, Me, 277°, 228°; Me, Et, Me, Me, 245°, 235°; Et, Et, Me, Me, 266°, 218°; Et, Me, Me, Et, 270°, —; Me, Et, Me, Et, 249°, 196°; Et, Et, Me, Et, 255°, 182°; Me, Et, Et, Me, 268°, 198°; Et, Et, Et, Me, 281°, 180—183°; Et, Et, Et, Et, 285°, 194°.

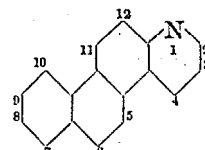
XIX. Solubilities of 2 : 8-dialkoxy-*N*-alkylacridones in H₂O, MeOH, EtOH, AcOH, and C₆H₆ are determined.
CH. ABS. (b)

Phenanthrene series. XIX. Naphthoquinolines synthesised from aminophenanthrenes.

E. MOSETTIG and J. W. KRUEGER (J. Org. Chem., 1938, 3, 317—339).—Naphthoquinolines are prepared from 3- (I) and 2-aminophenanthrene and 2-amino-9 : 10-dihydrophenanthrene (II). Structures of the products are proved mainly by degradation. The direction of ring-closure is compared with that in similar cases. (I) (prep. from the oxime of the Ac derivative by Ac₂O-AcOH-HCl), m.p. 140—142°, gives only naphtho[1 : 2-*f*]quinoline (IV) (45% yield) (cf. A., 1936, 1125). Reduction of (IV) by Sn-HCl or Na-EtOH or electrolytically is unsatisfactory. With H₂-PtO₂ in AcOH (IV) gives very slowly a mixture of the 1 : 2 : 3 : 4-H₄- (V) and 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12- or 1 : 2 : 3 : 4 : 5 : 6 : 1a : 4a-H₈-derivatives (VI); hydrogenation of (V) to (VI) is much more rapid. At 170° H₂-Cu-Cr₂O₃ gives only 45% of (IV) (cf. *loc. cit.*). (V) gives the *methiodide*, m.p. 185—187° (decomp.), of the 4-Me derivative, which with AgCl gives the *methochloride*, m.p. 174—176° (decomp.), pyrolysis of which gives a mixture containing mostly the 4-Me derivative, m.p. 77—78.5° (corr.) [*hydrochloride*, m.p. 215—217° (decomp.)]; the above-mentioned quaternary salts are reduced by Na-Hg in H₂O to 4- γ -dimethylamino-*n*-propylphenanthrene, an oil [*hydrochloride*, m.p. (anhyd.) 159—160° or (+EtOH) 125—127°; *methiodide*, m.p. 208—208.5° (corr.)]. Emde degradation of the *methiodide*, m.p. 275—280° (decomp.), of (VI) is slow and produces decomp. With glycerol and FeSO₄ in PhNO₂ (II)

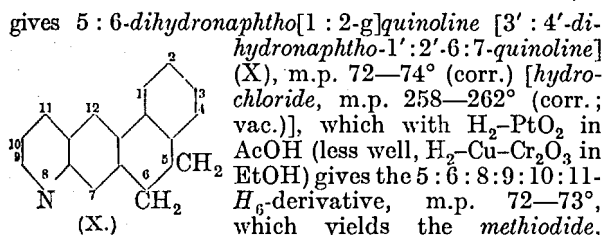


(IV.)



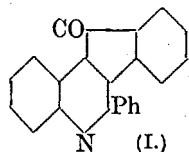
(VII.)

gives naphtho[2 : 1-*f*]quinoline [naphtho-2' : 1'-5 : 6-quinoline] (VII), m.p. 226—227° (corr.) [*hydrochloride*, m.p. 296—300° (vac.)], hydrogenated in presence of PtO₂ in AcOH or Cu-Cr₂O₃ in EtOH at 130—136°/162 atm. to the 1 : 2 : 3 : 4-H₄-derivative (VIII), m.p. 157—159° (corr.) [*hydrochloride*, m.p. 310—313° (decomp.); *methochloride*, m.p. 188—190°], but with the latter catalyst at 230°/217 atm. to the 1 : 2 : 3 : 4 : 5 : 6-H₆-derivative (IX), m.p. 115—116° [*hydrochloride*, m.p. 274—285° (corr.; vac.)], also obtained impure from (VIII) by H₂-PtO₂ in AcOH. (VIII) gives the *methiodide*, m.p. 204—205° (decomp.), of the Me derivative; this, when distilled in vac., gives the 1-Me derivative, m.p. 170—171° (corr.) [*hydrochloride*, m.p. 240—260° (decomp.)], of (VIII), and, when reduced by Na-Hg, gives a product (*hydrochloride*, m.p. 206—207°). Emde degradation of the corresponding methochloride gives 1- γ -dimethylamino-*n*-propylphenanthrene, an oil [*hydrochloride*, m.p. 195—200°; *picrate*, m.p. 164.5—166.5° (corr.)]. (IX) yields similarly the 1-Me derivative, m.p. 129—131° (*methiodide*, m.p. 193—195°, unstable in hot H₂O), and 1- γ -dimethylamino-*n*-propyl-9 : 10-dihydrophenanthrene [*hydrochloride*, m.p. 207—209°; *picrate*, m.p. 145.5—146.5° (corr.)]. By the Skraup synthesis (III)



m.p. 196—200° (decomp.), of its Me derivative and thence 3- γ -dimethylamino-n-propyl-9:10-dihydrophenanthrene (XI) [hydrochloride, m.p. 150—151° (corr.); picrate, m.p. 101.5—103° (corr.)]. With Pd-black in N_2 at 300—360° (X) gives naphtho[1:2-g]quinoline, m.p. 159—160° [hydrochloride, m.p. 280—295° (vac.)], hydrogenated (PtO₂; AcOH) to the 8:9:10:11- H_4 -derivative, an oil, which yields the methiodide, m.p. 203—205° (decomp.), of its 8-Me derivative, and thence 3- γ -dimethylamino-n-propylphenanthrene (XII) [hydrochloride, m.p. 160—162° (corr.); picrate, m.p. 150.5—151.5° (corr.); methiodide, m.p. 173—174° (163—164°); perchlorate, m.p. 84.5—89° (corr.)], also obtained in one experiment from (XI) by Pd in N_2 at 190—200°. 3- γ -Dimethylamino- α -hydroxy-n-propylphenanthrene hydrochloride and PCl₅ in CHCl₃ give 3- α -chloro- γ -dimethylaminopropylphenanthrene hydrochloride, double m.p. 150—155° and 238—240°, which with H_2 -Pd(OH)₂-CaCO₃ gives (XII). 2- γ -Dimethylamino-n-propylphenanthrene is unchanged by Na-Hg and Na-EtOH gives a mixture. 2-Acetyl-9:10-dihydrophenanthrene, (CH₂O)₃, and NHMe₂.HCl in hot iso-C₅H₁₁.OH give 2- β -dimethylaminopropionyl-9:10-dihydrophenanthrene, m.p. 70—71° (corr.) [hydrochloride, m.p. 162—163° (corr.)], hydrogenated (PtO₂; 60% EtOH) to 2- γ -dimethylamino- α -hydroxy-n-propyl-9:10-dihydrophenanthrene, m.p. 72—74° (corr.), the hydrochloride, m.p. 159—161° (corr.), of which with PCl₅ in CHCl₃ yields 2- α -chloro- γ -dimethylamino-n-propyl-9:10-dihydrophenanthrene hydrochloride, m.p. 214—216°, and thence 2- γ -dimethylamino-n-propyl-9:10-dihydrophenanthrene hydrochloride, m.p. 204—206° (corr.). R. S. C.

Polynuclear, condensed systems with heterocyclic rings. III. W. BORSCHÉ and O. VORBACH (Annalen, 1938, 537, 22—38; cf. A., 1937, II, 518, 519).—2:3-Diphenylquinoline-4-carboxyl chloride is



cyclised by AlCl₃ in PhNO₂ at 60° to 9-keto-4-phenyl-1:2-benzo-3-azafluorene (I), m.p. 263° (oxime, m.p. 254°; 2:4-dinitrophenylhydrazine, m.p. 320°), which does not appear to give a picrate. It is reduced by N₂H₄.H₂O at 200° in 20 hr. to 4-phenyl-1:2-benzo-3-azafluorene, m.p. 184° (picrate, m.p. 200°), also obtained by Sn powder with boiling AcOH-4N-HCl. Isatinic acid and CH₂PhAc give 3-phenyl-2-methyl- (II), decomp. 312°, and 2-benzyl-, m.p. 220° (decomp.), -quinoline-4-carboxylic acid. The chloride of (II) is transformed by AlCl₃ in PhNO₂ into 9-keto-4-methyl-1:2-benzo-3-azafluorene (III), m.p. 198° (oxime, m.p. 292°; 2:4-dinitrophenylhydrazine, m.p. 317°; picrate, m.p. 235°), also obtained from (II) and conc. H₂SO₄ at 100°. Condensation of (III) with the requisite aldehyde affords 4-styryl-, m.p.

185°, 4-p-methoxystyryl-, m.p. 199°, and 4-o-nitrostyryl-, m.p. 224°, -1:2-benzoazafluorene. (III) is reduced by N₂H₄.H₂O at 200° to 4-methyl-1:2-benzo-3-azafluorene, m.p. 133° (hydrochloride, decomp. 285°; picrate, m.p. 180°). CH₂Ph.COEt, obtained with β -hydroxy- α -diphenyl- β -ethylglutaric acid, m.p. 181° (decomp.), by the action of EtCOCl on CHPh(MgCl).CO₂Na, isatin, and KOH in EtOH at 100° yield 3-phenyl-2-ethyl- (IV), m.p. 302—303° (decomp.), and 2-benzyl-3-methyl- (V), m.p. 235—237°, -quinoline-4-carboxylic acid. Distillation of (IV) with Cu-bronze yields 3-phenyl-2-ethylquinoline, b.p. 200—203°/17 mm. (picrate, m.p. 177°), whilst (V) affords 2-benzyl-3-methylquinoline, b.p. 187—192°/15 mm. (picrate, m.p. 184°). The chloride of (IV) is cyclised to 4-ethyl-1:2-benzo-3-azafluorenone, m.p. 157—158° [sulphate, m.p. 255° (decomp.)], also obtained from (IV) and conc. H₂SO₄. 4-Ethyl-1:2-benzo-3-azafluorene has m.p. 101°. 3-Phenyl-2-benzylquinoline-4-carboxylic acid (Me ester, m.p. 101°) [whence 3-phenyl-2-benzylquinoline, m.p. 60°, b.p. 260—265°/2 mm. (picrate, m.p. 190°)] is converted by PCl₅ in POCl₃ at 100° into 9-keto-4-phenyl-1:2-benzo-3-azafluorene, m.p. 220° (2:4-dinitrophenylhydrazine, m.p. 308°); the acid and conc. H₂SO₄ at 80° yield 9-keto-4-benzyl-1:2-benzo-3-azafluorene- γ -sulphonic acid, m.p. 322°. 3-Phenyl-3-benzylquinoline-4-carboxylic chloride, AlCl₃, and C₆H₆ at 60° give 4-phenyl-1:2-benzo-3-aza-anthran-9-ol, m.p. 265° (picrate, m.p. 234°; Ac derivative, m.p. 197°), which does not react with 2:4-(NO₂)₂C₆H₃.NH.NH₂; the corresponding free acid and conc. H₂SO₄ at 80° appear to give a sulphonic acid, C₂₂H₁₅O₄NS, m.p. >360°. Isatin, KOH, and CO(CH₂.CH₂Ph)₂ give 3-benzyl-2- β -phenylethylquinoline-4-carboxylic acid, m.p. (anhyd.) 175° (hydrated) 120° [whence 3-benzyl-2- β -phenylethylquinoline, m.p. 98° (picrate, m.p. 198°; methiodide, m.p. 193°), transformed by PCl₅-POCl₃ into (?)-chloro-4- β -phenylethyl-1:2-benzo-3-aza-anthranol, m.p. 265° after softening at 255° (picrate, m.p. 244°), which does not react with 2:4-(NO₂)₂C₆H₃.NH.NH₂. 2- β -Phenylethylquinoline-4-carboxylic acid has m.p. 221°. Decarboxylation of (II) by Cu-bronze gives 3-phenyl-2-methylquinoline (VI), b.p. 207—209°/12 mm. (picrate, m.p. 170°; methiodide, m.p. 196°), which with the appropriate aldehyde and Ac₂O at 140° affords 3-phenyl-2-styryl-, m.p. 103°, -2-p-methoxystyryl-, m.p. 120°, and -2-o-nitrostyryl-, m.p. 120°, -quinoline. 2- β -Phenylethylquinoline (picrate, m.p. 130°; methiodide, m.p. 189°) has b.p. 216—218°/13 mm., m.p. 29—30°. Et₂C₂O₄ and (VI) condense to Et 3-phenylquinolyl-2-pyruvate, m.p. 160° (K derivative; picrate, m.p. 145°; 2:4-dinitrophenylhydrazine hydrochloride, decomp. 197°), from which the following are obtained: Et α -benzoyloxy-3-phenylquinolyl-2-acrylate, m.p. 117°; Et α -oximino- β -3-phenylquinolyl-2-propionate, m.p. 173°, and the corresponding acid (+H₂O), m.p. 141°; the anhydride of the acetyloximino-acid, C₂₀H₁₄O₃N₂, m.p. 147°, and the corresponding Bz derivative, m.p. 188°; 3-phenylquinolyl-2-acetonitrile, m.p. 93°. 2-Benzylquinoline, b.p. 212—213°/12 mm. (picrate, m.p. 155°; methiodide, m.p. 208°), gives an anisylidene derivative, isolated as its picrate, m.p. 225°. It is converted into Et phenyl-2-quinolylpyruvate, m.p. about 172° (K derivative), which does

not appear to form a picrate or a 2:4-dinitrophenyl-hydrazone. *Et* α -oximino- β -phenyl- β -quinolyl-2-propionate, m.p. 191°, and the corresponding acid, decomp. 164°, are described. H. W.

Formation of uramil from dialuric acid. D. DAVIDSON and H. SOLOWAY (J. Org. Chem., 1938, 3, 365—371).—Formation of uramil from alloxantin by the action of NH_4Cl involves formation of the imine and interaction thereof with dialuric acid to give uramil and alloxan, since formation of uramil from dialuric acid and NH_4Cl is catalysed by O_2 or alloxan. Uramil probably exists as the enol. R. S. C.

New azo-compounds and iodo-derivatives of histidine and histamine. W. DIEMAIR and H. FOX (Ber., 1938, 71, [B], 2493—2499).—*N*^a-Benzoylhistidine Me ester (I) and PhN_2Cl in 10% Na_2CO_3 yield di(benzeneazo)-*N*^a-benzoylhistidine (II), $\text{NH}\cdot\text{C}(\text{N}:\text{NPh})\text{CH}_2\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{H}$, converted by CH_3N_2 in $\text{MeOH-Et}_2\text{O}$ into the Me ester, m.p. 217°. Benzoylhistamine under similar conditions gives benzeneazo-*N*^a-benzoylhistamine (III), m.p. 186.5°. *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ gives *p*-nitrobenzeneazoglyoxaline, m.p. 248°, with glyoxaline and di-*p*-nitrobenzeneazo-*N*^a-benzoylhistidine, m.p. 160—161° (Me ester, m.p. 208°). Reduction of (II) with SnCl_2 and HCl gives a red aminohistidine hydrochloride, very sensitive to air, and much less stable than the simple aminoglyoxaline. Al-Hg is unsuitable as a reducing agent since it does not decolorise (II) completely. Reduction with catalytically excited H_2 confirms the constitution of (II) by the amount of gas absorbed. Rapid experiment in the absence of air leads to a red NH_2 -compound of *N*^a-benzoylhistidine which decomposes to red, oily smears when its purification or union with compounds which stabilise the NH_2 group is attempted. Reduction of (III) with SnCl_2 and HCl gives colourless crystals which decompose rapidly on exposure to air and do not yield a Bz compound. (I), 0.1*N*- NaOH-MeOH , and I afford monoiodo-*N*^a-benzoylhistidine Me ester (IV), m.p. 190°; monoiodo-*N*^a-benzoylhistidine has m.p. 208°. Both compounds are stable towards conc. alkalis and moist Ag_2O . (IV) couples with PhN_2Cl to (II), I being immediately eliminated. H. W.

Nickel catalyst in hydrogenation of 4-amino-5-cyano-2-methylpyrimidine. M. DELÉPINE (Bull. Soc. chim., 1938, [v], 5, 1539—1550; cf. A., 1938, II, 247).—4-Amino-2-methylpyrimidine-5-aldehyde (I), m.p. 192° [hydrochloride (+ H_2O , lost at 100°), m.p. 280—281° (decomp.); platinichloride (+ $2\text{H}_2\text{O}$, lost at 100° for 3 hr.); chromat; picrate, m.p. 220°; oxime; semicarbazone, m.p. 335—336° (decomp.); hydrazone, m.p. 296—297° (volatilises); compound with $\text{NHPh}\cdot\text{NH}_2$, m.p. 215°; internal salt, + H_2SO_3 (+ H_2O) (formula)], affords complexes, $[\text{C}_5\text{H}_4\text{N}_2\langle\text{CH}\cdot\text{CH}\rangle\text{M}]$, with Ni (+ $7\text{H}_2\text{O}$; 6 mols. lost at 100°), Co (+ $7\text{H}_2\text{O}$), and Cu (+ $6\text{H}_2\text{O}$); mechanism of formation, though the $5\text{-CH}_2\cdot\text{OH}$ compound, is discussed. With AgNO_3 , a compound of 2 mols. of (I) and 1 mol. of AgNO_3 , is obtained. 4-Amino-2-methyl-5-aminomethylpyrimidine gives a hydrochloride, + H_2O , m.p. 304—305° (decomp.). A. T. P.

Anomalous decomposition of the tetrazo-derivative of 2:2'-diamino-1:1'-dinaphthyl. IV. Reaction of *o*-(4:5-1':2'-naphth-3-pyrazolyl)cinnamic acid with thionyl chloride. A. CORBELLINI, C. BOTRUGNO, and F. CAPUCCI (R. Ist. lombardo Sci Lett., Rend., 1936, [ii], 69, 477—484; Chem. Zentr., 1937, i, 1420).—*cis-o*-(4:5-1':2'-Naphth-3-pyrazolyl)cinnamic acid (I) and boiling SOCl_2 give a chloride, $\text{C}_{20}\text{H}_{11}\text{ON}_2\text{Cl}$, m.p. $\sim 250^\circ$ (decomp.; darkens $\sim 200^\circ$), hydrolysed (5% NaOH) to an acid, $\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_2$, m.p. 273.5° (Me, m.p. 238°, Et, m.p. 234°, and isoamyl esters; amide, m.p. 274°), which contains 2 H less than (I) and affords *o*-(4:5-1':2'-naphth-3-pyrazolyl)benzoic acid, m.p. 266—268.5° (decomp.), when fused with KOH . Reduction (Zn dust, AcOH) of the acid (and esters) gives (I) (and esters). H. B.

Structure and properties of Pinacryptol-green. I. N. GORBATSCHIEVA and I. I. LEVKOEY (Photo-Kino Chem. Ind. U.S.S.R., 1936, 1, 59—63).—Reduction (SnCl_2) of the product from *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$ and (?) picryl chloride gives (?) 1:3-diamino-5-phenylphenazonium chloride (Pinacryptol-green). CH. ABS. (b)

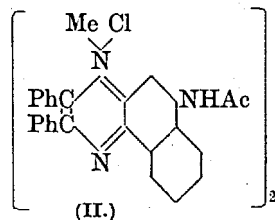
Derivatives of 3-carboline. R. H. FREAK and R. ROBINSON (J.C.S., 1938, 2013—2015).—Decomp. of 1:2'-pyridyl-1:2:3-benzotriazole in H_3PO_4 gives 3-carboline, which forms a methosulphate, m.p. 204—205°, and a methiodide, m.p. 208°. The methosulphate and NaOH yield 3-methyl-3-isocarboline, m.p. 138—139°, which behaves as a resonance hybrid, and with EtI affords 3-methyl-1-ethylcarbolinium iodide, m.p. 195°. 3-Carboline ethosulphate, m.p. 114—115°, similarly gives 3-ethyl-3-isocarboline, m.p. 102°, which with NaI yields 3-carboline ethiodide, m.p. 199—200°. 3-Ethyl-3-carboline on methylation affords 1-methyl-3-ethylcarbolinium iodide, m.p. 209.5°. Reduction of 3-carboline with Na-BuOH gives 3- γ -aminopropylindole. 1:2-Naphthylenediamine and 2-chloropyridine yield 3:2'-pyridyl- β -naphthaisotriazole, m.p. 159°, which with H_3PO_4 forms 9:10-benzo-3-carboline, m.p. 256° (picrate, decomp. 300°). F. R. S.

1:3-Diaza-anthraquinones.—See B., 1939, 18.

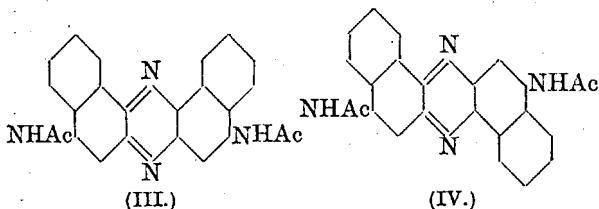
Azine dyes derived from naphthalene. S. MILHAÉLOV (Bull. Soc. chim., 1938, [v], 5, 1655—1664).—4-Acetamidonaphthylene-1:2-diamine (I) and phenanthra-9:10-quinone give the cryst. acetamido-azine, hydrolysed

by aq. H_2SO_4 to the azine, m.p. 309—313°. $(\text{COPh})_2$ gives the acetamido-azine, m.p. 244.2—245°, hydrolysed to the azine, $\text{C}_{24}\text{H}_{17}\text{N}_3$, m.p. 235°, which gives the salt (II). Atm. oxidation of (I) or condens-

ation of (I) with 4-acetamidonaphtha-1:2-quinone gives much of the azine (III) with some of the azine (IV), which are readily hydrolysed to the Ac-free azines, sensitive to NH_3 . 3-Acetamidonaphtha-1:2-quinone and (I) give a similar mixture of isomeric diacetamidazines. 4:5-Dihydroxy-*o*-benzoquinone and (I) give an acetamidoazine and thence the



free azine. 4-Hydroxynaphtha-1 : 2-quinone and (I) give two products; the mixture is hydrolysed



and the free azines are isolated as dihydrochlorides, $C_{20}H_{13}ON_3 \cdot 2HCl$. R. S. C.

γ -Triazines. XXXVII. Liebig and Wöhler's so-called trigenic acid : 2 : 4-diketo-6-methyltriazidine or cycloethylidenebiuret. A. OSTROGOVICH and G. OSTROGOVICH (Gazzetta, 1938, 68, 688—698).—Repeating the Liebig-Wöhler prep. (Annalen, 1846, 59, 296), cyanuric acid (I) is heated with MeCHO; the resulting "trigenic acid" is 2 : 6-diketo-6-methyltriazidine (cycloethylidenebiuret) (II) (cf. A., 1936, 616), m.p. 272—273°, mixed with unchanged (I), which is now removed as the Ba salt, and the sol. Ba derivative of (II) decomposed by CO_2 . Salts prepared from (II) are identical with those from the reduction product of dihydroxymethyltriazine (loc. cit.); the basic Hg salt, $C_5H_5O_2N_3(Hg \cdot OH)_2$, decomp. 250—252° (Ac₂ derivative), is also described. The Ac₂ derivative of (II) has new m.p. 175—176°.

E. W. W.

Heterocyclically substituted pyruvic esters.
III. Quinoxalyl-2-pyruvic esters and 3-methylquinoxalyl-2-pyruvic esters. W. BORSCHÉ and W. DOELLER (Annalen, 1938, 537, 39—52; cf. A., 1937, II, 32).—Addition of 2-methylquinoxaline to a solution of K and $Et_2C_2O_4$ in Et_2O -EtOH at 0° gives *Et* quinoxalyl-2-pyruvate (I), m.p. 161—162° [*K* derivative, picrate, m.p. 134°; methiodide, decomp. 176°; *O*-Bz derivative, m.p. 94—98°; oxime (II), m.p. 146—148°; 2 : 4-dinitrophenylhydrazones, m.p. 136—137°; hydrazones hydrate, $C_{11}H_{15}ON_4$, decomp. 225°]. It could not be smoothly hydrolysed to the corresponding acid and does not give characteristic condensation products with aromatic aldehydes. With $o-NH_2 \cdot C_6H_4 \cdot CHO$ it readily gives *Et* 3-2'-quinoxalylquinoline-2-carboxylate, m.p. 153—154°; the corresponding acid, decomp. about 181° (Na salt; Me ester, m.p. 172—173°), passes at 200—205° into 3-2'-quinoxalylquinoline, m.p. 214—215° (picrate, m.p. 238—239°; methiodide, decomp. 268—269°). $o-C_6H_4(NH_2)_2$ and (I) at 100° give 3'-hydroxy-2 : 2'-diquinoxalylmethane, m.p. 307—309°. Diazotised NH_2Ph and (I) yield *Et* $\alpha\beta$ -diketo- β -quinoxalyl-2-propionate β -phenylhydrazone, m.p. 158—160°, which gives only amorphous products when hydrolysed; the corresponding *p*-tolylhydrazone, m.p. 149—150°, is transformed by 5% KOH into an unidentified compound, in $C_{17}H_{12}O_2N_2$, decomp. 244—245°. Gradual addition of SeO_2 to 2-methylquinoxaline in xylene at 130° gives quinoxaline-2-aldehyde, m.p. 110° (phenylhydrazone, m.p. 229—230°; oxime, m.p. 197—198°). $PhCHO$, $p-C_6H_4Me \cdot NH_2$, and (I) in boiling EtOH slowly give 4 : 5-diketo-2-phenyl-1-*p*-tolyl-3-quinoxalyl-2-pyrrolidine, m.p. 283—285°; the corresponding β -naphthyl derivative decomposes at 290—292°. (II) is readily

hydrolysed by alkali but the resulting acid is purified with difficulty and is therefore converted directly by Ac_2O at 45° into quinoxalyl-2-acetonitrile (II), m.p. 116—117° (boiling Ac_2O gives α -cyano- α -2-quinoxalylacetone, m.p. 228—229°). $p-NO \cdot C_6H_4 \cdot NMe_2$ and (II) in boiling MeOH afford the *p*-dimethylaminoanil of quinoxalyl-2-glyoxylonitrile, m.p. 251°. With the requisite N_2 -compound (II) gives quinoxalyl-2-glyoxylonitrile *p*-tolylhydrazone, m.p. 187—188°, and *p*-anisylhydrazone, m.p. 188—190°. With $PhCHO$ in EtOH containing a little piperidine (II) yields α -2-quinoxalylcinnamonitrile, m.p. 146—147°; 4-methoxy- α -2-quinoxalylcinnamonitrile, m.p. 162—163°, and $\alpha\beta$ -di-2-quinoxalylacrylonitrile, m.p. 245°, are obtained similarly. $o-OH \cdot C_6H_4 \cdot CHO$ and isatin give respectively 3-2'-quinoxalylcoumarin, m.p. 196—197°, and 2-keto-3-2'-quinoxalylcyanomethene-2 : 3-dihydroindole, m.p. 306—308°. 2 : 3-Dimethylquinoxaline, $Et_2C_2O_4$, and KOEt yield *Et* 3-methylquinoxalyl-2-pyruvate (III), m.p. 129—130° (picrate, m.p. 140—141°; *O*-Bz derivative, m.p. 119—122°; oxime, m.p. 181—182°; 2 : 4-dinitrophenylhydrazone, m.p. 179—180°), hydrolysed to 3-methyl-2-quinoxalylpyruvic acid, decomp. 223—225° (*K* salt). (III) is unaffected by aromatic aldehydes (including $o-NH_2 \cdot C_6H_4 \cdot CHO$) and aromatic N_2 -compounds under the usual conditions. With $o-C_6H_4(NH_2)_2$ it gives 3'-hydroxy-3-methyl-2 : 2'-diquinoxalylmethane, decomp. 355°. 3-Methyl-2-quinoxalylacetonitrile, m.p. 131—133°, is converted into 3-methyl-2-quinoxalylglyoxylonitrile *p*-dimethylaminoanil, m.p. 183—184°, *p*-tolylhydrazone, m.p. 223—224°, and *p*-anisylhydrazone, m.p. 204°. α -3-Methyl-2-quinoxalylcinnamonitrile, m.p. 138°, and α -3-methyl-2-*p*-methoxyquinoxalylcinnamonitrile, m.p. 143°, are described.

H. W.

Dehydrogenation of pyridium and of neotropine : 8-substituted 6-amino-2 : 3-pyridino-7 : 8 : 9-triazoles. G. CHARRIER and M. JORIO (Gazzetta, 1938, 68, 640—651).—"Pyridium" (3-benzeneazo-2 : 6-diaminopyridine hydrochloride) in EtOH with aq. $CuSO_4$ and NH_3 is dehydrogenated to 6-amino-8-phenyl-2 : 3-pyridino-7 : 8 : 9-triazole (I) [6'-amino-2-phenylpyrido-2' : 3'-4 : 5-triazole] (cf. A., 1935, 226), m.p. 215° [hydrochloride; platinechloride; Ac derivative, m.p. 241—242°; (SO_3H)₂ derivative; $CH_2 \cdot CO_2H$ derivative, m.p. 242—243°]. With 1 : 2 : 4- $C_6H_3Cl(NO_2)_2$, (I) gives the 6-(2' : 3'-dinitroanilino)-derivative, m.p. 265—270°; and with CH_2O and $NaHSO_3$ forms a product, m.p. 275—280°. "Neotropine" (2 : 6-diamino-2'-*n*-butoxy-3 : 3'-azopyridine) in EtOH with aq. $CuSO_4$ and NH_3 yields 6-amino-8-(2'-*n*-butoxy-5'-pyridyl)-2 : 3-pyridino-7 : 8 : 9-triazole, m.p. 212°.

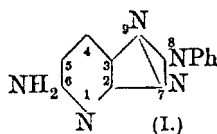
E. W. W.

Tetrabenztriazaporphins.—See B., 1939, 18.

Constitution of some naturally occurring, sensitising dyes. A. TREIBS (Strahlenther., 1938, 61, 658—663).—A discussion of the constitution of porphyrins.

H. W.

Preparation of adenosine.—See A., 1939, III, 197.



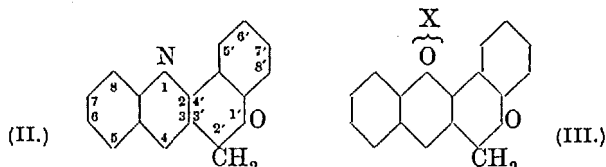
isoOxazole series. VI. Amino-derivatives of aliphatic type. A. QUILICO and L. PANIZZI (Gazzetta, 1938, 68, 625—640).—3-Methylisooxazole-5-carboxyl chloride, m.p. 39°, b.p. 89°/20 mm. (from the Na salt of the acid), yields, via the amide, 5-cyano-3-methylisooxazole (I), b.p. 174°, and, via the anilide, the 5-anilide iminochloride (II), m.p. 70—71°. 5-Methylisooxazole-3-carboxyl chloride similarly gives 3-cyano-5-methylisooxazole (III), m.p. 182—184°, and the 3-anilide iminochloride (IV), m.p. 70—73°. Anhyd. $\text{SnCl}_2\text{-HCl}$ in Et_2O , followed by 15—20% aq. NaOH , reduces (II) to (3-methyl-5-isooxazolylmethyl)aniline, m.p. 51—52° [Bz derivative, m.p. 86—87°; NO derivative, m.p. 74—75° (decomp.)]; similarly (IV) gives (5-methyl-3-isooxazolylmethyl)aniline [Bz derivative, m.p. 110°; NO -derivative, m.p. 67—68° (decomp.)]. In the same way, (I) and (III) are reduced to (3-methyl-5-isooxazolylmethyl)amine, b.p. 84—85°/5—8 mm. (hydrochloride, decomp. 221—222°; platinichloride, decomp. 211—216°; picrate, decomp. 179—181°; Bz derivative, m.p. 108°), and (5-methyl-3-isooxazolylmethyl)amine, b.p. 83°/5—8 mm. (hydrochloride, decomp. 202—203°; platinichloride, decomp. 203°; picrate, decomp. 179—181°; Bz derivative, m.p. 108.5—109.5°). 3-Phenyl-5-methylisooxazole-4-carboxylamide (A., 1938, II, 462) heated with P_2O_5 gives the corresponding 4-cyano-compound, m.p. 83.5—84.5°. E. W. W.

isoOxazole series. I. A. QUILICO and R. FUSCO. II. Halogen derivatives. A. QUILICO and R. JUSTONI (R. Ist. lombardo Sci. Lett., Rend., 1936, [ii], 69, 439—457, 587—601; Chem. Zentr., 1937, i, 1424—1425).—I. isoOxazoles are synthesised from, e.g., $\text{C}_6\text{H}_5\text{Cl}\cdot\text{N}\cdot\text{OH}$ (I) and $\text{COR}\cdot\text{CH}_2\text{X}$ ($\text{X} = \text{COR}, \text{CHO}, \text{CO}_2\text{Et}, \text{CN}$, etc.); other methods are reviewed. Thus (I) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in cold $\text{EtOH}\text{-NaOEt}$ give *Et* 5-amino-3-phenylisooxazole-4-carboxylate, m.p. 124°, hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to the free acid (II), decomp. 181° [Ag salt; amide, m.p. 170—171°, from (I) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$], and by dil. KOH to 5-amino-3-phenylisooxazole, m.p. 110—111° (CHPh ., m.p. 135—136°, anisylidene, m.p. 148°, and cinnamylidene, m.p. 161°, derivatives). Azo-dyes are obtained from (II) and PhN_2Cl or $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$, and (II) is degraded by dil. HCl at 130° to COPhMe , NH_2OH , NH_3 , and CO_2 . 4-Cyano-3:5-diphenylisooxazole, m.p. 130—131°, similarly obtained from (I) and $\text{COPh}\cdot\text{CH}_2\cdot\text{CN}$ or from $\text{CHBz}_2\cdot\text{CN}$ and NH_2OH , is stable towards heat, alkalis, dil. acids, oxidising agents, and $\text{NHPh}\cdot\text{NH}_2$; short treatment with conc. H_2SO_4 at 150° gives small amounts of (probably) 3:5-diphenylisooxazole-4-carboxylamide, m.p. 210° (two modifications; cf. Betti *et al.*, A., 1922, i, 52).

II. 3:5-Dimethyl- and 3- and 5-methyl- (III) isooxazoles with Cl_2 and Br form additive compounds, which when heated or exposed to sunlight lose HHal to give the 4-halogeno-derivatives [those of (III) are converted by $\text{EtOH}\text{-NaOEt}$ into $\text{COMe}\cdot\text{CHHal}\cdot\text{CN}$]. The following are described: 4-chloro- (IV), b.p. 135—135.5°, and 4-bromo- (V), b.p. 147—148°, 5-methyl-, 4-bromo-3-methyl-, b.p. 142.5—144.5°, and 4-chloro-, b.p. 150—150.5°, and 4-bromo-, b.p. 169°, 3:5-dimethyl-isooxazole.

$\text{COMe}\cdot\text{CHCl}\cdot\text{CN}$ [Na salt from (IV) and $\text{EtOH}\cdot\text{NaOEt}$] with $\text{NHPh}\cdot\text{NH}_2$ and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in H_2O gives β -benzeneazo-, m.p. 81°, and β -p-nitrobenzeneazo- (VI), m.p. 90°, -crotononitrile, respectively; the former is also obtained from $\text{COMe}\cdot\text{CHBr}\cdot\text{CN}$ [from (V)]. Boiling conc. HCl converts (VI) into (probably) β -2-chloro-4-nitrophenylhydrazinocrotononitrile, m.p. 149—150°. H. B.

Chromenoquinolines and chromenobenzopyrylium salts. P. PFEIFFER and G. VON BANK (J. pr. Chem., 1938, [ii], 151, 312—318).—Chromanone (I) and $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ are condensed by



2N-NaOH in cold MeOH to chromenoquinoline (II), m.p. 121.5°, which dissolves in conc. H_2SO_4 to a yellow solution with green fluorescence. It gives a well-cryst. perchlorate, m.p. 280—281° after darkening at about 260°, *H* sulphate without definite m.p., and chloride, m.p. 237° (decomp.). It is oxidised by H_2O_2 and boiling 2N-HCl to a compound, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}$, m.p. 259°. Analogously, 7-methoxychromanone affords 7'-methoxychromenoquinoline, m.p. 118—119°, which dissolves in conc. H_2SO_4 to a yellow solution with a green to blue fluorescence [perchlorate, softens and commences to decompose at 270°; nitrate, m.p. 173° (decomp.); chloride, m.p. 232° (decomp.)]. 7-Hydroxychromanone gives 7'-hydroxychromenoquinoline, m.p. 160° (slight decomp.) after softening at 145° [perchlorate, m.p. 295° (decomp.) after softening and darkening at 290°]. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and (I) in MeOH are transformed by HCl at 0° followed by HClO_4 into chromenobenzopyrylium perchlorate (cf. III) (corresponding platinichloride, decomp. about 220°). 7'-Methoxychromonobenzopyrylium perchlorate, m.p. 232° (decomp.) after softening at 210°, and platinichloride, blackens at 220°, are described.

H. W.

Dialkylthiazolidinediones. W. J. DORAN and H. A. SHONLE (J. Org. Chem., 1938, 3, 193—197).— $\text{CS}(\text{NH}_2)_2$ with $\text{CRR}'\cdot\text{Br}\cdot\text{COCl}$ or with $\text{CRR}'\cdot\text{Br}\cdot\text{CO}_2\text{H}$ and NaOH in EtOH gives 2-imino-4-keto-5:5-diethyl-, new m.p. 237—238°, 5-ethyl-5-n-propyl-, m.p. 220—222°, 5-ethyl-5-isobutyl-, m.p. 225—227°, 5-ethyl-5-sec-butyl-, m.p. 215—216°, and 5-ethyl-5- α -methyl-n-butyl-thiazolidine, m.p. 229—231°, hydrolysed by dil. HCl to the corresponding 2:4-diketo-5:5-dialkylthiazolidines, m.p. 78—78.5°, an oil, m.p. 70—72°, and 105—107°, respectively, which have short sedative and anaesthetic action, but cause tremors or convulsions. α -Bromo- γ -methyl- α -ethyl-n-valeric, b.p. 121—125°/2.5 mm., and α -bromo- β -methyl- α -ethyl-n-hexzoic acid, b.p. 120—125°/1 mm., are prepared.

R. S. C.

Indigoid vat dyes of the isatin series. III. 3-Indole-2'-(4'-methyl)thionaphtheneindigos. S. K. GUHA (J. Indian Chem. Soc., 1938, 15, 501—508; cf. A., 1937, II, 393).—3-Hydroxy-4-methylthionaphthen and isatin in $\text{AcOH}\text{-HCl}$ afford 3-

indole-2'-(4'-methyl)thionaphthenindigo [3-keto-2-oxindolidene-4-methyldihydrothionaphthen] (I). The respective substituted isatins give similarly the 5-chloro-, 5-bromo-, 5:7-dibromo-, 5-bromo-7-nitro-, and 5:7-dinitroindole derivatives of (I). 3-Hydroxythionaphthen and 5:7-dinitroisatin give 3-(5:7-dinitro)indole-2'-thionaphthenindigo. The dyeings on cotton and wool, and absorption spectra, are compared with those of the isomeric 5'- and 6'-Me compounds; change in shade is produced in the same way as observed in other series (cf. A., 1938, II, 243, 455). A. T. P.

Ox- and thi-azole derivatives [polarising substances].—See B., 1939, 106.

Thiazole derivatives.—See B., 1939, 106.

Heterocyclically substituted pyruvic esters.
IV. Pyruvic esters from 1-methylbenzoxazole. 1-methylbenzthiazole, and 1-substituted 2-methylbenziminazoles. W. BORSCHKE and W. DOELLER (Annalen, 1937, 537, 53—66).—1-Methylbenzoxazole (I), $\text{Et}_2\text{C}_2\text{O}_4$, and KOEt in EtOH- Et_2O afford *Et* 1-benzoxazolylpyruvate (II),

$\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, m.p. 69° (oxime, m.p. 127—128°; 2:4-dinitrophenylhydrazone, m.p. 194°), which does not give a picrate or a methiodide. It is hydrolysed to 1-benzoxazolylpyruvic acid, decomp. 154° (K salt), converted by NH_2OH into the compound, $\text{C}_9\text{H}_8\text{O}_5\text{N}_2$, m.p. 199°, and oxidised by $\text{NaOH}\cdot\text{H}_2\text{O}_2$ to 1-benzoxazolylacetic acid, decomp. 116°, which gives (I) when distilled. (II) and the requisite N_2 -compound yield *Et* $\alpha\beta$ -diketo- β -1-benzoxazolylpropionate β -phenylhydrazone, m.p. 131—132°, and β -p-tolylhydrazone, m.p. 165°. With PhCHO and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in boiling EtOH (II) affords 4:5-diketo-2-phenyl-1-p-tolyl-3-1'-benzoxazolylpyrrolidine, m.p. 288—290°; the corresponding 1- β -naphthyl derivative has m.p. 302—305°. When heated with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (II) affords 3-hydroxy-2-quinoxalyl-1'-benzoxazolylmethane, m.p. about 330°. (II) is converted by $o\text{-NH}_2\text{C}_6\text{H}_4\cdot\text{CHO}$ at 100° into *Et* 3-1'-benzoxazolylquinoline-2-carboxylate, m.p. 144—145°; the corresponding acid, decomp. 174°, is decarboxylated to 3-1'-benzoxazolylquinoline, m.p. 178—179° (picrate, m.p. 203°). 1-Methylbenzthiazole (III) and $\text{Et}_2\text{C}_2\text{O}_4$ give *Et* 1-benzthiazolylpyruvate (IV), m.p. 166° (picrate, m.p. 155—156°; 2:4-dinitrophenylhydrazone, m.p. 194—195°, and its hydrochloride; oxime, m.p. 147°). (IV) is hydrolysed to 1-benzthiazolylpyruvic acid, m.p. 173° (K salt), oxidised (H_2O_2 in alkaline solution) to the unstable 1-benzthiazolylacetic acid, characterised by decarboxylation to (III). With the appropriate N_2 -compound (IV) yields *Et* $\alpha\beta$ -diketo- β -1-benzthiazolylpropionate β -phenylhydrazone, m.p. 146—147° [hydrolysed to the corresponding acid, m.p. 243° (decomp.)], and p-tolylhydrazone, m.p. 143—144° [corresponding acid, m.p. 207° (decomp.)]. SeO_2 oxidises (III) to benzthiazole-1-aldehyde, m.p. 65° (oxime, m.p. 186—187°; phenylhydrazone, m.p. 204—205°). 4:5-Diketo-2-phenyl-1-p-tolyl-, decomp. 270—272°, and 4:5-diketo-2-phenyl-1- β -naphthyl-, decomp. 286—288°, -3-1'-benzthiazolylpyrrolidine are described. With $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ at 100° (IV) yields 3-hydroxy-2-quinoxalyl-1-benzthiazolylmethane, m.p. 318—320°. *Et*

3:1'-benzthiazolylquinoline-2-carboxylate, m.p. 158—159°, from (IV) and $o\text{-NH}_2\text{C}_6\text{H}_4\cdot\text{CHO}$ at 100°, is hydrolysed and decarboxylated to 3:1'-benzthiazolylquinoline, m.p. 198—199° (picrate, m.p. 223—224°; methiodide, decomp. 152—155°). The oxime, decomp. about 200°, of 1-benzthiazolylpyruvic acid is transformed by warm Ac_2O into 1-benzthiazolylacetonitrile (V), m.p. 98—100°, and converted by boiling Ac_2O into α -cyano- α -1-benzthiazolylacetone, m.p. 229°. $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and (V) in MeOH afford 1-benzthiazolylglyoxylonitrile p-dimethylaminoanil, m.p. 251—254°. With the appropriate N_2 -compound in AcOH (V) yields 1-benzthiazolylglyoxylonitrile p-tolylhydrazone, m.p. 193—195°, and p-anisylhydrazone, m.p. 169—170°. With aromatic aldehydes or isatin in EtOH containing piperidine (V) gives α -1-benzthiazolylcinnamonnitrile, m.p. 121—122°, p-methoxy- α -1-benzthiazolylcinnamonnitrile, m.p. 145°, $\alpha\beta$ -di-1-benzthiazolylacrylonitrile, m.p. 211—213° and 2-keto-3-cyano-1'-benzthiazolylmethene-2:3-dihydroindole, m.p. about 240°. Attempts to esterify (V) with boiling $\text{HCl}\cdot\text{MeOH}$ led to (III). 1:2-Dimethylbenziminazole and $\text{Et}_2\text{C}_2\text{O}_4$ slowly give *Et* 1-methyl-2-benziminazolylpyruvate, m.p. 154—156° (K compound), in very modest yield. With some uncertainty 1-phenyl-2-methylbenziminazole (VI) and $\text{Et}_2\text{C}_2\text{O}_4$ afford *Et* 1-phenyl-2-methylbenziminazolylpyruvate, m.p. 151—152° (picrate, decomp. 185—186°), which gives a green colour with FeCl_3 . $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and (VI) at 200° yield 1-phenyl-2-phthalidenemethenylbenziminazole, $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{CH}\cdot\text{C}\langle\text{C}_6\text{H}_4\rangle\text{CO}$, m.p. 280—281°. H. W.

New heterocyclic syntheses. IV. [Five-membered rings containing 2 N and S or Se.] R. FUSCO and C. MUSANTE (Gazzetta, 1938, 68, 665—681; cf. A., 1938, II, 340).— $\text{NHPh}\cdot\text{N}\cdot\text{CPhCl}$ (I), 2:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CPhBr}$ (II), and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$ (III) heated with $\text{NaS}\cdot\text{CS}\cdot\text{OEt}$ (IV) in EtOH give respectively 2-thion-3:5-diphenyl-, m.p. 151—152°, -5-phenyl-3-(2':4'-dibromophenyl)-, m.p. 129°, and -5-carbethoxy-3-(p-nitrophenyl)-1:3:4-thiodiazoline, m.p. 151°. With $\text{KS}\cdot\text{CO}_2\text{Et}$ (V), (I), (II), and (III) give respectively 2-keto-3:5-diphenyl-, 2-keto-5-phenyl-3-(2':4'-dibromophenyl)- (cf. loc. cit.), and 2-keto-5-carbethoxy-3-(p-nitrophenyl)-1:3:4-thiodiazoline (VI), m.p. 91°. With KCNS , (I), (II), and (III) give respectively 2-imino-3:5-diphenyl-, m.p. 111—113° [hydrochloride, m.p. 250° (decomp.)], -5-phenyl-3-(2':4'-dibromophenyl)-, m.p. 70° (hydrobromide, m.p. 265°), and -5-carbethoxy-3-(p-nitrophenyl)-1:3:4-selenodiazoline, m.p. 178—179° [hydrochloride, m.p. 216° (decomp.)]. The NO-derivative, m.p. 124° (decomp.), of the last, when heated in xylene, gives 2-keto-5-carbethoxy-3-(4'-nitrophenyl)-1:3:4-selenodiazoline, m.p. 97—98°, which with dil. H_2SO_4 liberates Se. With KCNS , (III) gives 2-imino-5-carbethoxy-3-p-nitrophenyl-1:3:4-thiodiazoline, m.p. 175° [hydrochloride, m.p. 213° (decomp.)], of which the NO-derivative, m.p. 110° (decomp.), in boiling xylene gives 3-carbethoxy-1-p-nitrophenyl-1:2:4-triazol-5-one, m.p. 235°, hydrolysed (boiling aq. KOH) to the 5-carboxy-compound, m.p. 300° (decomp.) (softening at 260°). With $\text{CPhCl}\cdot\text{N}\cdot\text{OH}$, (IV) and (V) give only PhNCS ,

whilst KCNSe gives a product, m.p. 188°, and NPh:C(SH)NH₂ gives PhNCS and PhNCO.

E. W. W.

Transformations of quinidine and quinine. E. LÉGER (J. Pharm. Chim., 1939, [viii], 29, 12—32).—A review.

Salts of alkaloids. U. P. BASU and (in part) M. ROY (J. Indian Chem. Soc., 1938, 15, 513—515).—Attempts are made to obtain less toxic salts of alkaloids for therapeutic use. *Emetine d-camphor-β-sulphonate*, m.p. 203—204°, is less toxic than the hydrochloride. *Ephedrine camphorsulphonate* has m.p. 173—174°. Quinine affords a *camphorsulphonate*, m.p. 218—219°, mandelate, m.p. 189—190°, 2-*hydroxy-3-naphthoate*, m.p. 149—150°, and 1:1'-*methylene-2:2'-dinaphthyl-3:3'-dicarboxylate*, m.p. 199—200°.

A. T. P.

Addition of organomagnesium halides to ψ-codeine types. IV. Nuclear-substituted morphine derivatives. L. SMALL, S. G. TURNBULL, and H. M. FITCH (J. Org. Chem., 1938, 3, 204—232; cf. A., 1936, 1277).—Compounds of ψ-codeine type, e.g., enol esters of 6-CO-derivatives and dihydrothebaine, react with MgAlkHal with opening of the oxide ring and introduction of an alkyl group. Sometimes isomerides are formed; this isomerism may be due to stereoisomerism of CHAlk at C₍₅₎, or to substitution at C₍₅₎ and C₍₇₎, but it cannot be due to stereoisomerism of CHAlk at C₍₇₎, since, e.g., methyl dihydrocodeinone enol acetate (I) also reacts with MgRX, showing that the grouping O-CH·C(OAc)·Alk· is present and thus that Alk is at C₍₇₎. Reaction of dihydrocodeine enol acetate (prep. described), m.p. 152—153.5°, with MgMeI is improved. *isoMethyl dihydrothebainone hydriodide*, m.p. 259—260° (decomp.), [α]_D²⁵ -28° in H₂O, *methiodide*, +H₂O and anhyd., m.p. 194—196° (decomp.), [α]_D²⁵ -18.6° in H₂O, *hydrochloride*, +1.5H₂O and anhyd., sinters at 182°, m.p. 191—193° (decomp.), [α]_D²⁵ -122.1° in H₂O, and *hydriodide*, +H₂O, sinters at 205°, m.p. 209—210° (decomp.), [α]_D²⁵ -102.1° in H₂O, are described. *isoMethyl dihydrothebainone* (II) with <2 mols. of Br gives its 1-Br-derivative, m.p. 237—239°, [α]_D²⁵ -66.2° in abs. EtOH [reduced catalytically to (II)], as well as 1-bromoisomethyl dihydrocodeinone, and with 2.5 mols. of Br, followed by alkali and hydrogenation, gives (?) 7-ketoisomethyl dihydrothebainone, m.p. 172°, [α]_D²⁵ -67.3° in EtOH, or, after sublimation, m.p. 258—259°, [α]_D²⁵ -97.4° in EtOH. *isoMethyl dihydrocodeinone* is hydrogenated (PtO₂) in EtOH to *isomethyl dihydrocodeine*, +0.25H₂O, m.p. 103—104°, [α]_D²⁵ -126.9° in EtOH [*salicylate*, m.p. 235—237° (decomp.), [α]_D²⁵ -87.3° in EtOH; *methiodide*, m.p. 252—254° (decomp.), [α]_D²⁵ -56.8° in H₂O]. Dihydrothebaine and MgEtI (freed from EtI by NMe₃) in C₆H₆ give *ethyl-* (III), m.p. 190.5—191.5°, [α]_D²⁵ +10.9° in EtOH [*hydrochloride*, m.p. 280—282° (decomp.), [α]_D²⁵ +17.8° in H₂O; *hydriodide*, m.p. 253—255° (decomp.), [α]_D²⁵ +14.0° in H₂O], and *isoethyl dihydrothebainone*, m.p. 188—189°, [α]_D²⁵ -36.2° in EtOH, cryptophenolic (*hydriodide*, +H₂O, m.p. 191—193°, [α]_D²⁵ -4.1° in H₂O; *methiodide*, +0.5H₂O, sinters at 218°, m.p. 237—240°, [α]_D²⁵ -5.8° in H₂O). With Br-AcOH, followed by treatment with NaOH, (III) gives 1-

bromoethyl dihydrothebainone, m.p. 201.5—202.5°, [α]_D²⁵ -6.8° in EtOH [reduced catalytically to (III)], and oily 1-bromoethyl dihydrocodeinone, which is hydrogenated to *ethyl dihydrocodeinone* (IV), m.p. 163—164°, [α]_D²⁵ -100.9° in EtOH [*methiodide*, +0.5H₂O, m.p. 255—257° (decomp.), [α]_D²⁵ -48.8° in H₂O; enol acetate, m.p. 129—130°, [α]_D²⁵ -124.1°], and thence to *ethyl dihydrocodeine*, an oil, [α]_D²⁵ -84.8° in EtOH [*perchlorate*, m.p. 275—276°, [α]_D²⁵ -60.5° in abs. EtOH; *hydriodide*, m.p. 274—275°, [α]_D²⁵ -50.6° in H₂O]. Hydrolysis of (IV) by 48% HBr gives *ethyl dihydro morphinone*, m.p. 213—214°, [α]_D²⁵ -103.5° in abs. EtOH [*hydriodide*, m.p. 285—286° (decomp.), [α]_D²⁵ -49.1° in H₂O; *methiodide*, +0.5H₂O and anhyd., m.p. 263—265° (decomp.), [α]_D²⁵ -42.2° in H₂O]. Dihydrothebaine and MgRBr in C₆H₆ give *isopropyl dihydrothebainone* (V), m.p. 217.5—219.5°, [α]_D²⁵ -31° in CHCl₃ [*hydrochloride*, m.p. 273—275°, [α]_D²⁵ -18.3° in H₂O; *hydrobromide*, m.p. 277—277.5°, [α]_D²⁵ -12.6° in H₂O; *salicylate*, m.p. 165—185°, [α]_D²⁵ -8.9° in COMe₂; *perchlorate*, m.p. 236—238°, [α]_D²⁵ -16.0° in COMe₂; *fumarate*; *succinate*; *hydriodide*; *picrate*; *oxime*, +2H₂O, double m.p. 130—137° (partly) and 199—201°, [α]_D²⁵ +13.5° in EtOAc (*hydrochloride*, m.p. 213—215°, decomp. 228°, [α]_D²⁵ +43.8° in H₂O); 1:5-Br₂-derivative *hydrobromide*, +2H₂O and anhyd., m.p. 230—232°, [α]_D²⁵ -2.7° in EtOH], *n-amyl dihydrothebainone* (VI), m.p. 153—155°, sublimates at 150°/high vac., [α]_D²⁵ -12.8° in EtOH (*hydrochloride*, +H₂O, m.p. 203—205°, [α]_D²⁵ +2.8° in EtOH; *hydrobromide*, m.p. 223—224.5°, [α]_D²⁵ +1.5° in EtOH; *hydriodide*, m.p. 238—239°, [α]_D²⁵ -1.4° in EtOH; *perchlorate*, +0.5H₂O, m.p. 235—236°, [α]_D²⁵ -2.13° in EtOH; *sulphate*, +2.5H₂O, m.p. 95—105°, [α]_D²⁵ 0 in EtOH; *oxime*, +1.5H₂O, m.p. 113—115°, [α]_D²⁵ +18.6° in EtOH), *benzyl dihydrothebainone* (VII), m.p. 227—229°, [α]_D²⁵ -51.6° in CHCl₃ [*hydrochloride*, m.p. 243—244° (decomp.), [α]_D²⁵ -29° in H₂O; *oxime*, m.p. 135—142°, [α]_D²⁵ +5.5° in CHCl₃], *phenyl dihydrothebainone* (VIII), m.p. 230—232°, [α]_D²⁵ -165.9° in CHCl₃ [*perchlorate*, m.p. 201° (decomp.), [α]_D²⁵ -97.6° in COMe₂; *methiodide*, m.p. 245—248° (decomp.), [α]_D²⁵ -96.5° in EtOH; *oxime*, m.p. 198—200°, [α]_D²⁵ -106.7° in EtOH], and *isophenyl dihydrothebainone* (IX), m.p. 213—215°, [α]_D²⁵ +34.8° in CHCl₃ (*methiodide*, m.p. 214—215°, [α]_D²⁵ 0 in EtOH; *oxime*, m.p. 230—232°, [α]_D²⁵ -157° in EtOH). With Br, followed by 10N-NaOH, (V) gives 1-bromoisopropyl dihydrocodeinone, m.p. 164—167°, [α]_D²⁵ -79.4° in COMe₂, hydrogenated (colloidal Pd) in AcOH-KOAc to *isopropyl codeinone*, m.p. 175—177°, sublimates at 155°/high vac., [α]_D²⁵ -110.5° in EtOH [*hydrobromide*, m.p. 202—203°, [α]_D²⁵ -58.3° in H₂O; *hydriodide*, +H₂O, m.p. 196—198°, [α]_D²⁵ -67.2° in EtOH; *methiodide*, m.p. 274—275° (decomp.), [α]_D²⁵ -66.0° in COMe₂; *oxime*, m.p. 224—226°, [α]_D²⁵ -25.0° in EtOH]; this is not reduced catalytically, by Na₂S₂O₄, or SnCl₂, but with Zn-Hg-HCl gives (V), and with 48% HBr gives *isopropyl dihydro morphinone*, m.p. 236—238°, sublimates at 180°/high vac., [α]_D²⁵ -107.5° in EtOH [*hydrochloride*, +H₂O, m.p. 340—341° (decomp.), [α]_D²⁵ -64.2° in H₂O; *hydrobromide*, m.p. 215—220°, [α]_D²⁵ -56.4° in H₂O; *hydriodide*, +H₂O, m.p. 199—201°, [α]_D²⁵ -61.5° in COMe₂; *perchlorate*, + (?) 1.25H₂O, m.p. 168—170°, [α]_D²⁵ -69.9° in EtOH],

unaffected by H_2 -Pd or $-\text{PtO}_2$, reduced by Zn-Hg-HCl to a (?) bimol. product, decomp. $277-280^\circ$, $[\alpha]_D^{25} -117.6^\circ$ in EtOH. With Br, followed by 10N-NaOH , (VI) gives 1-bromoamylidihydro-thebainone, m.p. $241-242^\circ$, $[\alpha]_D^{25} -30.6^\circ$ in EtOH, and -codeinone, m.p. $143-145^\circ$, $[\alpha]_D^{24} -76.7^\circ$ in EtOH [oxime, $+0.25\text{H}_2\text{O}$, double m.p. $121-123^\circ$ (partly) and $170-174^\circ$, $[\alpha]_D^{24} -29.7^\circ$ in EtOH], and thence amylidihydrocodeinone, m.p. $153-155^\circ$, $[\alpha]_D^{25} -9.3^\circ$ in EtOH [picrate, m.p. $174-177^\circ$ (sinters at 130°), $[\alpha]_D^{24} -52.8^\circ$ in COMe_2 ; styphnate, $+0.75\text{H}_2\text{O}$, m.p. $142-145^\circ$ (decomp.), $[\alpha]_D^{25} -45.4^\circ$ in COMe_2 ; salicylate], and amylidihydro-morphinone, $+0.5\text{H}_2\text{O}$, m.p. $113-116^\circ$ (decomp.), $[\alpha]_D^{25} -97.3^\circ$ in EtOH [hydrochloride, m.p. $322-325^\circ$ (decomp.), $[\alpha]_D^{25} -63.9^\circ$ in H_2O ; hydrobromide, $+\text{H}_2\text{O}$, m.p. $189-190^\circ$, $[\alpha]_D^{25} -66.0^\circ$ in EtOH; hydriodide, $+\text{H}_2\text{O}$, m.p. $182-184^\circ$, $[\alpha]_D^{25} -59.8^\circ$ in EtOH], not hydrogenated catalytically and giving amorphous products by Clemmensen's method. Similarly (VII) gives 1-bromo-x-benzylidihydro-thebainone, m.p. $230-232^\circ$, $[\alpha]_D^{25} -59.4^\circ$ in EtOH, and -codeinone, m.p. $167-168^\circ$, $[\alpha]_D^{25} -101.4^\circ$ in EtOH (salicylate; fumarate; perchlorate; sulphate), benzylidihydro-codeinone (X), an oil, b.p. 160° /high vac., $[\alpha]_D^{25} -114.3^\circ$ in CHCl_3 , and -morphinone (hydrochloride, $+\text{H}_2\text{O}$, m.p. $241-242^\circ$, $[\alpha]_D^{24} -100.6^\circ$ in H_2O), and an isomeride of (X), m.p. $166-167.5^\circ$, $[\alpha]_D^{24} -439^\circ$ in CHCl_3 . When similarly treated, (VIII) gives oily Br-compounds and thence phenylidihydro-codeinone, m.p. $149-151^\circ$, $[\alpha]_D^{24} -166.2^\circ$ in EtOH, and -morphinone, m.p. $278-280^\circ$ (decomp.), $[\alpha]_D^{24} -164.5^\circ$ in COMe_2 [hydrochloride, m.p. $334-337^\circ$ (decomp.), $[\alpha]_D^{24} -126.9^\circ$ in H_2O ; hydrobromide, $+1.25\text{H}_2\text{O}$, m.p. $281-284^\circ$, $[\alpha]_D^{25} -97.4^\circ$ in COMe_2 ; hydriodide, $+\text{H}_2\text{O}$, m.p. $273-276^\circ$, $[\alpha]_D^{25} -95.1^\circ$ in COMe_2]. With MeI-NaOMe-MeOH (IX) gives isophenylidihydrothebainone Me ether methiodide, m.p. $264-265^\circ$, $[\alpha]_D^{24} +49.3^\circ$ in EtOH, converted by AgCl into the unstable methochloride, m.p. $239-243^\circ$, which at $200-205^\circ$ /high vac. yields 6-keto-3:4-dimethoxy-5- or -7-phenyl-5:6:7:8-tetrahydrophenanthrene, m.p. $227-230^\circ$, $[\alpha]_D^{22} -130^\circ$ in C_6H_6 . By way of oily intermediates (IX) gives oily isophenylidihydrocodeinone, which is not demethylated by HBr , but gives instead a rearrangement product, $\text{C}_{24}\text{H}_{25}\text{O}_3\text{N}$, m.p. $189-190^\circ$, $[\alpha]_D^{24} -127.5^\circ$ in EtOH. Prep. of (V) gives also by demethylation some dihydromorphinone enol acetate, m.p. $233-235^\circ$, $[\alpha]_D^{24} -206.5^\circ$ in EtOH [hydrochloride, m.p. $309-310^\circ$ (decomp.), $[\alpha]_D^{25} -180.6^\circ$ in H_2O ; hydriodide, m.p. $274-275^\circ$ (decomp.), $[\alpha]_D^{25} -140.5^\circ$ in H_2O ; benzoate, m.p. $229-230^\circ$, $[\alpha]_D^{25} -150.7^\circ$ in EtOH; salicylate, $+0.25\text{H}_2\text{O}$ (retained at 130°), m.p. $268-270^\circ$, $[\alpha]_D^{25} -130.8^\circ$ in COMe_2 ; methiodide, $+\text{H}_2\text{O}$, m.p. $259-261^\circ$, $[\alpha]_D^{25} -123.6^\circ$ in COMe_2], hydrolysed by cold, conc. HCl to dihydromorphinone, methylated (CH_3N_2) to dihydrothebaine, and obtained in poor yield also from dihydrothebaine by NaOMe-MeOH at $125-140^\circ$. With MgMeI in C_6H_6 (I) or its iso-isomeride gives dimethylidihydrothebainone (XI), m.p. $199-202^\circ$, $[\alpha]_D^{28} +3.52^\circ$ in EtOH (hydrochloride; oxime, m.p. about $70-90^\circ$), and a compound X (fumarate). With Br in AcOH (XI) gives a (?) perbromide and thence a Br-compound (not isolated), converted by NaOH into impure bromodimethylidihydrothebainone, m.p. $218-221^\circ$, cryptophenolic [reduced to (XI)]. ψ -Codeine Me ether (prep.

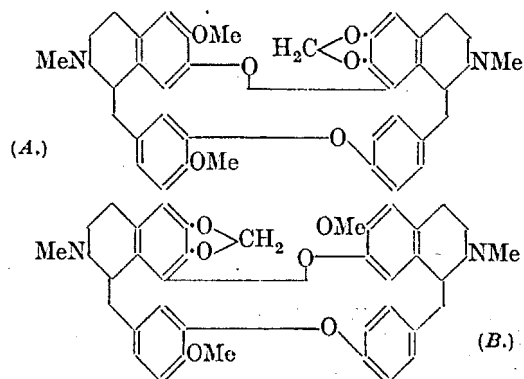
from α -chlorocodide by MeOH , which also causes much rearrangement to β -chlorocodide) and MgMeI in Et_2O give methylidihydro- ψ -codeine Me ether, m.p. $182.5-183^\circ$, sublimes at 150° /high vac., $[\alpha]_D^{23} +121.0^\circ$ in EtOH [hydrochloride, m.p. $247-251^\circ$ (decomp.), $[\alpha]_D^{25} +125.9^\circ$ in H_2O ; hydriodide, m.p. $256-257^\circ$ (decomp.), $[\alpha]_D^{25} +91.5^\circ$ in EtOH; perchlorate, m.p. $285-287^\circ$ (decomp.), $[\alpha]_D^{23} +103.1^\circ$ in EtOH; methiodide, m.p. $273-276^\circ$ (decomp.), $[\alpha]_D^{25} +98.1^\circ$ in EtOH]; in Pr^2O much of a substance, $\text{C}_{19}\text{H}_{27}\text{O}_3\text{N}$, m.p. $132-132.5^\circ$, sublimes at 110° /high vac., $[\alpha]_D^{25} -57.4^\circ$ in EtOH, is also formed. Most of the m.p. were determined in vac. R. S. C.

Mitraspecine, new alkaloid from *Mitragyna speciosa*, Korthals. P. DENIS (Bull. Acad. roy. Belg., 1938, [v], 24, 653-658).—The bark of *M. speciosa* contains 5%, and the wood 0.2%, of mitraspecine, $\text{C}_{25}\text{H}_{27}\text{O}_2\text{N}_2(\text{OMe})_3$, m.p. $244-245^\circ$, $[\alpha]_D^{25} -59.15^\circ$ in CHCl_3 (picrate, m.p. 136°). The extraction and pptn. and colour reactions are described.

A. LI.

Sinomenium and Cocculus alkaloids. XLVIII. Constitution of cepharanthine. H. KONDO and I. KEIMATSU (Ber., 1938, 71, [B], 2553-2560).—Purest cepharanthine (I) with C_6H_6 of crystallisation is $\text{C}_{37}\text{H}_{39}\text{O}_6\text{N}_2 \cdot 1.25\text{C}_6\text{H}_6$, m.p. 103° (decomp.). The solvent-free alkaloid is a yellow, amorphous powder, m.p. $145-155^\circ$, $[\alpha]_D^{20} +277^\circ$ in CHCl_3 . It contains 2 OMe, CH_2O_2 , and 2 NMe; OH, CO, and $\text{CO}\cdot\text{O}$ are absent. The first stage of the Hofmann degradation of (I) gives mainly the optically inactive cepharanthine- α -methine (I), $\text{C}_{39}\text{H}_{42}\text{O}_6\text{N}_2 \cdot 3\text{H}_2\text{O}$, m.p. $98-100^\circ$, with some optically active cepharanthine- β -methine, $\text{C}_{39}\text{H}_{42}\text{O}_6\text{N}_2 \cdot \text{H}_2\text{O}$, m.p. $183-184^\circ$, $[\alpha]_D^{27} +58^\circ$ in CHCl_3 . (I) gives a methiodide, m.p. $305-306^\circ$ (decomp.), which in the second stage of the degradation affords NMe₃ and de-N-cepharanthine, $\text{C}_{35}\text{H}_{36}\text{O}_7 \cdot 0.5\text{MeOH}$, m.p. about 210° (decomp.). Oxidation of (I) with KMnO_4 gives 6-methoxy-3:4'-dicarboxydiphenyl ether, m.p. 305° . Ozonisation of (I) in 25% AcOH at 0° and reduction of the product in presence of Pt-black yields 6-methoxy-3:4'-dialdehyddiphenyl ether, m.p. $77-78^\circ$, and 2-methoxy-2':3'-methylenedioxy-5:6'-dialdehydo-4:5-di- β -dimethylaminoethyldiphenyl ether, the methiodide, m.p. $217-220^\circ$ (decomp.), of which is degraded (Hofmann) to 2-methoxy-2':3'-methylenedioxy-5:6'-dialdehydo-4:5'-divinyldiphenyl ether (II), m.p. $166-168^\circ$ [dioxime, m.p. $181-182^\circ$ (decomp.)]. The same products are obtained from the methohydroxide of (I). Hydrogenation (Pt-black in EtOH- COMe_2) leads to 2-methoxy-2':3'-methylenedioxy-5:6'-dialdehydo-4:5'-diethyldiphenyl ether, m.p. $160-161^\circ$ (disemicarbazone, m.p. 218°). This is reduced (Clemmensen) to 2-methoxy-2':3'-methylenedioxy-5:6'-dimethyl-4:5'-diethyldiphenyl ether (III), m.p. $88-89^\circ$. 5-Hydroxy-4-methoxy-2-ethyltoluene (IV), b.p. $111-112^\circ/7\text{ mm.}$, m.p. 57.5° , is converted into 6-bromo-5-hydroxy-4-methoxy-2-ethyltoluene, b.p. $165-170^\circ/11\text{ mm.}$, m.p. $48.5-49^\circ$. This is transformed into its acetate, m.p. $67-68^\circ$, which with $\text{Ac}_2\text{O-HBr}$ ($d\ 1.78$) at $115-120^\circ$ gives 6-bromo-4:5-diacetoxy-2-ethyltoluene, m.p. $150-151^\circ$ after softening at 120° , whence (CH_3SO_4 and NaOH in $\text{COMe}_2\text{-H}_2\text{O}$)

6-bromo-4 : 5-methylenedioxy-2-ethyltoluene, m.p. 55—58° (V). When heated with Cu powder and $\text{Cu}(\text{OAc})_2$



at 165—200°, (IV) and (V) give (III). (I) is therefore A or B. H. W.

Organo-arsenic compounds. VIII. Synthesis of arsindole derivatives from phenylacetylene. IX. Synthesis of succinylphenylarsine. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1938, **15**, 495—497; 498—500).—VIII. CPhCH and AsPhCl_2 at 140—150° for 7 hr. (probably through the adduct, $\text{CPhClCH} \cdot \text{AsPhCl}$) afford 3-chloro-1-phenylarsindole, b.p. 165—175°/10 mm. (picrate, m.p. 115—116°; mercurichloride, m.p. 232—233°; methiodide, m.p. 152—153°; ethiodide, m.p. 161°), oxidised (H_2O_2) to o-carboxydiphenylarsinic acid, m.p. 166°.

IX. $(\text{CH}_2\text{COCl})_2$ and $\text{AsPhCl}_2 \cdot \text{Na} \cdot \text{C}_6\text{H}_5 \cdot \text{EtOAc}$ afford succinylphenylarsine, b.p. 119—120°/10 mm. (picrate, m.p. 117°; mercurichloride, m.p. 245°; methiodide, m.p. 176°; ethiodide, m.p. 165—167°), reduced by $\text{Na} \cdot \text{PhMe} \cdot \text{EtOH}$ to phenylcyclotetramethylenearsine, b.p. 125—130°/15 mm. A. T. P.

Hydrolysis of some arsphenamines. S. ORLIĆ (Arh. Hemiju, 1938, **12**, 153—172).—Max. hydrolysis of p-arsanilic acid takes place in 0.08N-NaOH, at 160°, and of o-arsanilic acid in 0.4N-NaOH, at 130—160°; m-arsanilic acid is resistant to hydrolysis at p_H 2—10 (90 min. at 200°). 4 : 4'-Diaminodiphenylarsinic acid is hydrolysed at 100° and 130° in acid solution (max. hydrolysis in 0.6N-HCl. Arsenobenzenes decompose as follows: $3\text{AsR} \cdot \text{AsR} + 3\text{H}_2\text{O} \rightarrow 4\text{As} + \text{As}_2\text{O}_3 + 6\text{RH}$ ($\text{R} = p\text{-C}_6\text{H}_4 \cdot \text{NH}_2$, 4 : 3- $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{NH}_2$); $3\text{AsR}_2 \cdot \text{AsR}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{As} + 2\text{As}_2\text{O}_3 + 12\text{RH}$ ($\text{R} = p\text{-C}_6\text{H}_4 \cdot \text{NH}_2$). These compounds are more resistant to hydrolysis in neutral and alkaline than in acid media, at 140—180°. R. T.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative degree of electronegativity of organic radicals. III. M. S. KHARASCH, H. PINES, and (Miss) J. H. LEVINE (J. Org. Chem., 1938, **3**, 347—354; cf. A., 1932, 409).—Cleavage of HgPhEt by $\text{HCl} \cdot \text{EtOH}$, $\text{HBr} \cdot \text{EtOH}$, $\text{HBr} \cdot \text{AcOH}$, $\text{HBr} \cdot \text{C}_6\text{H}_5$, $\text{HI} \cdot \text{AcOH}$, or $\text{HI} \cdot \text{C}_6\text{H}_5$ gives in all cases only HgEtHal . Cleavage of HgRR' by HCl proves the following orders of relative electronegativity: $p\text{-C}_6\text{H}_4\text{F} > \text{Ph} > p\text{-C}_6\text{H}_4\text{Cl}$, o-, m-, or $p\text{-C}_6\text{H}_4\text{Br}$, m- $\text{C}_6\text{H}_4\text{F}$; Ph , m- $\text{C}_6\text{H}_4\text{Cl} > m\text{-C}_6\text{H}_4 \cdot \text{CF}_3$; $\text{CH}_3\text{Ph} > o\text{-}$, m-, or $p\text{-C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2$; o- = m- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}_2$. The

following are described: m-, m.p. 243°, and p-fluoro-, m.p. 291°, p-chloro-, m.p. 238°, and m-trifluoromethyl-phenylmercuric chloride, m.p. 151°; o-, m.p. 115°, and m-chlorobenzylmercurichloride, m.p. 141°; di-o-chlorobenzylmercury, m.p. 100°; phenyl-m-, m.p. 107—111°, and p-fluoro-, m.p. 115—118°, p-chloro-, m.p. 172—200°, o-, m.p. 73—75°, m-, an oil, and p-bromo-, m.p. 151—175°, and m-trifluoromethylphenylmercury, m.p. 100—103°; m-chlorophenyl-m-trifluoromethylphenylmercury, m.p. 130—143°; benzyl-o-, an oil, m-, an oil, and p-chlorobenzylmercury, m.p. 80—82°; o-chlorobenzyl-m-, an oil, and p-chlorobenzylmercury, m.p. 98—129°. R. S. C.

Acetylation of proteins by keten. I. Method. Results with antidiphtheritic serum. G. SANDOR and H. GOLDIE (Bull. Soc. Chim. biol., 1938, **20**, 1130—1146).—A convenient apparatus for the production of keten is described. Acetylation is effected at $\sim p_H$ in the presence of octyl alcohol, and the serum is buffered with NaOAc , aq. NaOH being added at intervals to avoid acidification. It is advisable to introduce the serum gradually to avoid the formation of a clot. OH groups are not affected until at least 90% of the NH_2 -groups are acetylated. Characteristic modifications of the physico-chemical properties of the proteins occur. The flocculating power of antidiphtheritic serum towards the toxin disappears when 17—19% of the NH_2 -groups are acetylated, the antitoxic power and original specificity when 70—80% are acetylated, and the anaphylactogenic power when $\sim 20\%$ are acetylated. P. G. M.

Ashing of organic matter with bromine + nitric acid. H. WAELSCH and A. DIMTER (Mikrochim. Acta, 1938, **3**, 201—203).—Org. material is repeatedly evaporated ($\sim 160^\circ$) to dryness in a quartz vessel with fuming HNO_3 saturated with Br. 0.5 c.c. of serum, or 0.5 g. of brain, or 0.1 g. of filter-paper can be ashed in 60—90 min., and the method is quicker than that using $\text{HNO}_3 + \text{H}_2\text{O}_2$. In determining K', the last traces of NH_3 can be removed by treatment of the residue from the ashing with aq. $\text{NaOH} + \text{Br}$. L. S. T.

Determination of halogens in organic substances by the method of ter Meulen. W. THEILACKER and E. GESSNER (Angew. Chem., 1938, **51**, 892—893).—Minor modifications of the apparatus and method of ter Meulen (A., 1928, 724) are described. With substances which char readily, the low vals. obtained may be improved by mixing with $(\text{HCO}_2)_2\text{Ni}$. J. D. R.

Micro-determination of halogens in organic substances using filter beakers. E. ABRAHAMCZIK and F. BLÜMEL (Mikrochim. Acta, 1938, **3**, 185—189).—The Pregl tube with its layer of asbestos is replaced by the Schwarz-Bergkamf beaker, which is more const. in wt. ($\sim 4 \mu\text{g.}$) than the filter-tube. Also, the time required for a determination is shortened. L. S. T.

Catalyst for the determination of nitrogen by the Kjeldahl method.—See A., 1939, I, 96.

Preparation of hydriodic acid suitable for alkoxyl and Friedrich-Kjeldahl nitrogen determinations.—See A., 1939, I, 92.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1939.

Occurrence of free radicals during organic reactions. G. WITTIG (Angew. Chem., 1939, 52, 89—95).—A consideration of the following reactions in the gas phase: thermal and photochemical decomp. of MeCHO and homologous aldehydes, of COMe₂ and homologous ketones, of (NMe)₂ and CH₂N₂, of CH₄ and homologues; photohalogenation; action of Na on alkyl and aryl iodides. Review of the following reactions in solution: occurrence of CPh₃; benzidine transformation; isomerisation of tetraphenylsuccinodinitriles; decomp. of thermolabile azo-compounds and peroxides; photolysis of aliphatic ketones; additive reactions of olefines; photohalogenation of CHPh:CH·CO₂H; formation of (CH₂·OH)₂ from C₂H₄; autoxidation of tetraphenylxylylene and of CPh₃; polymerisation of unsaturated compounds such as CH₂:CHCl, C₂H₄, CHPh:CH₂, CPh₂:CH₂, and butadiene. H. W.

Attempts to prepare the methylene radical by the thermal decomposition of hydrocarbons. F. O. RICE (J. Amer. Chem. Soc., 1939, 61, 213).—By using a long hot wire and long Te mirrors, Te₂Me₂ is obtained from CH₄ and other hydrocarbons. CH₂ is unstable, readily giving Me. R. S. C.

New catalytic methods of synthesis of hydrocarbons. V. N. IPATIEV (Bull. Soc. Chim. Yougoslav., 1938, 9, 73—88).—A lecture. R. T.

Thermal stability of butane and isobutane. G. R. SCHULTZE and H. WELLER (Oel u. Kohle, 1938, 14, 998—1011).—The C₄H₁₀ used in previous work on its thermal decomp. (B., 1937, 20) was a mixture of *n*- and *iso*-C₄H₁₀. Pure *n*- or *iso*-C₄H₁₀, either alone or mixed with N₂, was passed through an electrically-heated SiO₂ tube (contact times 0.3—1.3 sec.). By extrapolation to zero contact time the primary decomp. reactions at 700° were found to be (a) *n*-C₄H₁₀ → C₄H₈ + H₂ (15%), *n*-C₄H₁₀ → C₃H₆ + CH₄ (54%), *n*-C₄H₁₀ → 2C₂H₄ + H₂ (16%), and *n*-C₄H₁₀ → C₂H₄ + C₂H₆ (13%); and (b) *i*-C₄H₁₀ → *i*-C₄H₈ + H₂ (52%), and *i*-C₄H₁₀ → C₃H₆ + CH₄ (48%). The variation of these with temp. (672—738°) and the effect thereon of the addition of N₂ are also recorded. It is concluded that chain reactions are involved. A. B. M.

Organic peroxide formed during the decomposition, by oxidation, of saturated hydrocarbons. K. IVANOV (Acta Physicochim. U.R.S.S., 1938, 9, 421—452).—Oxidation data have been obtained for cyclohexane at 316° and 328°, C₇H₁₆ at 255°, and *iso*-C₇H₁₆ at 295°. Non-volatile peroxides, C₇H₁₄O₇ and C₄H₈O₄, were obtained from the first compound and C₃H₆O₄ from the second and third.

The properties and possible structures of these peroxides and the oxidation mechanism are discussed.

C. R. H.

Oxidation of unsaturated hydrocarbons by hydrogen peroxide in presence of pervanadic acid. I. General course of the reaction and primary oxidation products. W. TREIBS (Ber., 1938, 72, [B], 7—10).—The oxidations are conveniently effected in COMe₂ with pervanadic acid as catalyst and indicator. The reaction of very resistant hydrocarbons is accelerated by sunlight but it is uncertain whether this is a true photocatalysis. The presence of trimeric acetone peroxide has never been detected but it is possible that a monomeric peroxide is an unstable intermediate of the reaction. Usually there is an induction period which is more pronounced with increasing purity of the hydrocarbon. The primary products of the catalysed H₂O₂ oxidation of olefines are α -oxides and α -unsaturated alcohols. The yield of the former increases with increasing concn. of the solution and with diminishing temp. The best results are obtained with normal hydrocarbons with terminal double linking. The oxides of some cycloolefines (pinene; Δ^4 -carene) are very unstable; these terpenes contain a 4- or 3-membered ring in conjugation to a double linking. These oxides immediately add H₂O with fission of the rings and production of unsaturated glycols. Caryophyllene gives a very stable α -oxide in 80% yield. $\alpha\beta$ -Unsaturated alcohols arise in very small amount by the oxidation of aliphatic olefines but are the main product from cycloolefines without side-chains (cyclohexene, tetrahydronaphthalene). If side-chains are present the course of the reaction depends on their position. Under drastic conditions the unsaturated alcohols are transformed into oxide-alcohols. Oxidation of alcohols to ketones is not effected by H₂O₂ or only with very great difficulty. $\alpha\beta$ -Unsaturated ketones and certain aldehydes are transformed by H₂O₂ into their peroxides. H. W.

Stability of co-ordinated ethylene hydrocarbons. A. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 307—310; cf. A., 1938, I, 43).—CHPh:CH₂ displaces C₂H₄ in Pt complexes. All ethylenic hydrocarbons are displaced by CO. Cossa's salt may be used as a reagent for C₂H₄ in gaseous mixtures. O. D. S.

Bromination of trimethylethylene. W. E. VAUGHAN and F. F. RUST (J. Amer. Chem. Soc., 1939, 61, 215—216).—The course of the reaction between CMe₂:CH₂ and Cl₂ depends greatly on the temp. and surface. Whereas at 109° in presence of CaCl₂ only 19% of HCl is liberated, at 70° 93% of

substitution occurs; much of the HCl formed adds to produce Bu^+Cl . Reaction of CMe_2CHMe is also complex, which invalidates the thermal data of Conn *et al.* (A., 1939, I, 28).

R. S. C.

Bromination of trimethylethylene. J. B. CONN, G. B. KISTIAKOWSKY, and E. A. SMITH (J. Amer. Chem. Soc., 1939, 61, 216—217).—Side reactions (cf. preceding abstract) occur only slightly under the authors' conditions (A., 1939, I, 28) and do not invalidate the results.

R. S. C.

Sodium saccharin as a reagent for the identification of alkyl halides. L. L. MERRITT, jun., S. LEVEY, and H. B. CUTTER (J. Amer. Chem. Soc., 1939, 61, 15—16).—Alkyl halides are characterised by condensing with Na saccharin in hot, aq. $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{OBu}$. MeCl , EtCl , $(\text{CH}_2\text{Cl})_2$, branched-chain and *tert.* chlorides do not react. *N*-iso-Propyl-, m.p. 134° , -*n*-, m.p. 38 — 39.5° , -iso-, m.p. 75° , and sec.-butyl-, m.p. 81° , -*n*-amyl-, m.p. 58° , and -allyl-, m.p. 99° , -saccharin, are prepared.

R. S. C.

Reactivity of carbon tetrachloride. H. J. HOFMANN (Angew. Chem., 1939, 52, 96—99).—Exposure of mixtures of CCl_4 and NH_2Ph to diffused daylight speedily causes the production of Cl^\cdot . In the dark the mixture appears to be stable but it is very sensitive to ultra-violet light. Irradiation of mixtures of CCl_4 and H_2O for 24 hr. does not appear to cause the formation of HCl, whilst in absence of NH_2Ph the change $2\text{CCl}_4 \rightarrow \text{C}_2\text{Cl}_6 + \text{Cl}_2$ does not occur. The products of the interaction of NH_2Ph and CCl_4 are $\text{CO}(\text{NHPh})_2$, *p*-aminobenzoic acid- NN' -diphenylamidine, m.p. 196° , and its hydrochloride, m.p. 280° , a compound $\text{C}_{19}\text{H}_{18}\text{N}_3\text{Cl}$, grey-green leaflets, m.p. 248° , a substance, (?) $\text{C}_{33}\text{H}_{25}\text{ON}_5$, red needles, m.p. 248° , azobenzene, and $\text{NH}_2\text{Ph} \cdot \text{HCl}$. Air is without influence on the change, which is not caused by the free NH_2 of NH_2Ph since NPhMe_2 is also active. CCl_4 can react with complex hydrocarbons if reactive positions are present in the mol. Conversely, reactivity with CCl_4 can be used in the detection of active positions in the mol. Reaction occurs also with products from mineral oils, the vigour of the change with oils of similar origin increasing from gas oil to cylinder oil. Exhaustive treatment with H_2SO_4 removes from the oils the components with groups reactive towards CCl_4 so that white oil does not react with CCl_4 . Reaction with CCl_4 can lead to errors in quant. analysis.

H. W.

Polymerisation of chloroprene as revealed by the Raman effect.—See A., 1939, I, 150.

Action of mineral acids on primary nitro-paraffins. S. B. LIPPINCOTT and H. B. HASS (Ind. Eng. Chem., 1939, 31, 118—120).—85% H_2SO_4 (1 mol.) is introduced into boiling EtNO_2 (or PrNO_2) (1 mol.) and the mixture boiled gently for 8 hr. [temp. rises to 117° (140°)] to give AcOH (or EtCO_2H), NH_4OH , and some NH_3 . PrNO_2 (1 mol.) and 100% H_2SO_4 (1 mol.) mixed at room temp. and heated carefully to 60° , kept at 50 — 60° for 16 hr., then at 95 — 100° for 5 hr., give $\text{OH} \cdot \text{CHEt} \cdot \text{N} \cdot \text{OH}$, m.p. 92.5 — 93.5° . Equimols. of BuNO_2 (or Bu^sNO_2) and 85% H_2SO_4 at 140° , then refluxed for 2 hr. (8 hr.) [temp. rises to 158° (154°)], give PrCO_2H (or $\text{Pr}^s\text{CO}_2\text{H}$)

(90% yields), with NH_2OH and NH_3 . Steam-distillation affords unchanged nitroparaffin and fatty acid [determined by titration with alkali (neutral-red indicator)] and a residue containing NH_2OH .

A. T. P.

Action of caustic alkali and of alkaline salts on alcohols. E. E. REID, H. WORTHINGTON, and A. W. LARCHAR (J. Amer. Chem. Soc., 1939, 61, 99—101).— MeOH , EtOH , Pr^sOH , Bu^sOH , Bu^tOH , and $\text{CMeEtBu}^s\text{OH}$ are treated with aq. NaOH and KOH in various proportions at 320 — 380° . The reaction, $\text{CH}_2\text{R} \cdot \text{OH} + \text{NaOH} \rightarrow \text{RCO}_2\text{Na} + 2\text{H}_2$, is almost quant. under some conditions (e.g., excess of alkali and at least some H_2O). Under other conditions, the reaction, $2\text{CH}_2\text{R} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{CH}_2\text{R} \cdot \text{CH}_2 \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{OH}$, occurs largely; it is effected with moderate yields by use of org. K or Na salts.

R. S. C.

***n*-Amyl deuterolcohol and ethyl deuteriothiol.**—See A., 1939, I, 143.

Action of sulphur in catalytic hydrogenations at high pressure.—See A., 1939, I, 151.

Preparation of glycols from ethylene hydrocarbons. H. MOUREU, M. DODÉ, and (MME.) DODÉ (Mém. Poudres, 1938, 28, 252—264).—Methods used for preparing glycols may be used for preparing the homologues of C_2H_4 . Hydrolysis of the monochlorohydrin with NaHCO_3 gives good yields but the solutions are very dil., and contain considerable amounts of NaCl , difficult to remove. An alternative method consists in converting the monochlorohydrins into the corresponding oxides, which are then transformed into glycols. This intermediate stage permits the separation of the components of mixtures of C_2H_4 , C_3H_6 , and C_4H_8 .

W. J. W.

Unsaponifiable matter from liver oils. I. Chimyl alcohol. Z. NAKAMIYA (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 837—852).—Sukoso-liver oil yields 6% of unsaponifiable matter, separated by fractionation of the acetates into chimyl alcohol (diacetate, m.p. 22° ; dibenzoate; di-3:5-dinitrobenzoate, m.p. 58 — 59° ; diphenylurethane, m.p. 100 — 100.5° ; anthraquinone-2-carboxylate, m.p. 71 — 73°), batyl alcohol (anthraquinone-2-carboxylate, m.p. 79 — 80°), and a small quantity of skesyl alcohol, $\text{C}_{17}\text{H}_{34}\text{O}(\text{OH})_2$, m.p. 64 — 65° (diphenylurethane, m.p. 79°). Since chimyl iodide with AgOAc gives cetyl alcohol, chimyl alcohol is glycerol monocetyl ether.

A. Li.

Induced peroxide formation during the bromination of olefines. W. BOCKEMÜLLER and L. PFEUFFER (Annalen, 1939, 537, 178—196).—When exposed to O_2 and Br vapour, cyclohexene, $\text{CH}_2 \cdot \text{CHPh}$, $\text{CH}_2 \cdot \text{CPh}_2$, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2\text{Cl}$ (I), or $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2\text{Br}$ (II) absorbs both Br and O_2 in ratios which depend on the olefine, temp., and solvent (if any). The products are peroxides. That from (II) is isolated as an oil (impure) and is probably $(\text{CH}_2\text{Br} \cdot \text{CHMe})_2\text{O}_2$, since reduction (TiCl_3 , SO_2 , or HI) gives $\text{CH}_2\text{Br} \cdot \text{CHMe} \cdot \text{OH}$ and thermal decomp. gives mainly $\text{CO}(\text{CH}_2\text{Br})_2$ with less $\text{COMe} \cdot \text{CH}_2\text{Br}$, H_2O , HBr , and $\text{C}_3\text{H}_5\text{Br}_3$. Alkaline H_2O_2 and Pr^sSO_4 give only $\text{Pr}^s\text{O}_2\text{H}$, but $\text{Pr}^s\text{O}_2\text{H}$ and alkaline Me_2SO_4 give *Me Pr*^s peroxide, b.p. 53 — 54° , which at 300° or

in paraffin at 200° gives CH_2O , COMe_2 , and H_2O . Thermal decomp. of the crude peroxide from (I) gives $\text{COMe}\cdot\text{CH}_2\text{Cl}$ and HBr with less $\text{COMe}\cdot\text{CH}_2\text{Br}$ and HCl . HgPr^β_2 and O_3 give COMe_2 and HgO . R. S. C.

Reaction of thiol compounds with aliphatic olefines. V. N. IPATIEV and R. S. FRIEDMAN (J. Amer. Chem. Soc., 1939, 61, 71—74).— AlkSH or AcSH adds to olefines contrary to Markovnikov's rule, but H_2S adds in accordance with it. An excess of H_2S gives mainly mercaptans, an excess of olefine gives mainly thioethers. Yields increase with branching of the chain. The following are reported. Bu^β (?) Bu^γ , b.p. 152—156°, Et Bu^β (compound, X_2HgCl_2 , m.p. 107—108°), Et iso- (compound, X_2HgCl_2 , m.p. 86—87°), and sec-iso-amyl , b.p. 150—152.5°/751 mm. (compound, X_2PdCl_2 , m.p. 92.5—94°), and $\text{Bu}^\alpha \text{ Bu}^\beta$ (compounds, X_2HgCl_2 , m.p. 105—106°, and X_2PdCl_2 , m.p. 73.5°), sulphide. *tert.*- $\text{C}_5\text{H}_{11}\text{SH}$, b.p. 98—100° (lit., 78°, 97°) [Hg^{++} salt, m.p. 59—60° (lit., 157°)]. Bu^β , new b.p. 151—152°/744 mm., *iso.*, b.p. 175—177°/748 mm., and *sec-iso-amyl thioacetate*, b.p. 75—76°/30 mm. R. S. C.

Halogen derivatives of triethylsulphonylmethane. E. SAMÉN (Arkiv Kemi, Min., Geol., 1938, 12, B, No. 51, 7 pp.).—Interaction of Br and $\text{CH}(\text{SO}_2\text{Et})_3$ (I), m.p. 218—220° (corr.) (lit. 212°), yields *bromotriethylsulphonylmethane* (II), m.p. 134—135° (corr.), which is a strong acid, oxidises HI to I , and decomposes N_2H_4 quantitatively to N_2 . Similarly *chlorotriethylsulphonylmethane*, m.p. 143—144°, is formed from (I) and Cl_2 in H_2O . (II) is decomposed by HBr to (I) and Br ; it is shown colorimetrically that the equilibrium $(\text{I}) + \text{Br}_2 \rightleftharpoons (\text{II}) + \text{HBr}$ is established in HBr solution. J. D. R.

Esters of sulphurous, chlorosulphinic, and chlorosulphonic acids. I. W. GERRARD (J.C.S., 1939, 99—103).—Interaction of BuOH , SOCl_2 , and $\text{C}_5\text{H}_5\text{N}$ (1 : 1 : 1 mol.) at 0° yields $\text{Bu}^\alpha\text{SO}_3$ in 80% yield, increased to 87% by carrying out the reaction in Et_2O . Similarly, *n*-amyl alcohol and *Et* lactate yield respectively *n*-amyl and α -carbethoxyethyl sulphite. When the above reactions are carried out at higher temp. and in presence of excess of $\text{C}_5\text{H}_5\text{N}$ (2—3 mols.), the alkyl chloride and sulphite are produced. The alkyl chloride is formed by catalytic decomp. of the primarily formed chlorosulphinate by $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$. Bu^α chlorosulphinate (I) and *Et* α -chlorosulphinoxypropionate (II) when heated with $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ yield BuCl and $\text{CHMeCl}\cdot\text{CO}_2\text{Et}$, respectively. Interaction of HCO_2H and (II) yields *Et* α -formoxypropionate, b.p. 69—70°/18 mm., α^β_{18} —6.38°, but no CO . Similarly (I), Bu^β , *Et*, and *iso-amyl* chlorosulphinates with HCO_2H give the appropriate formate, HCl , and SO_2 , but no CO , which affords a method of detection of SOCl_2 (which with HCO_2H yields CO) in presence of a chlorosulphinate. SOCl_2 in Et_2O with PhOH at —5° yields *Ph* chlorosulphinate, b.p. 100.5—101°/18 mm. J. D. R.

Reaction of esters with sodium in liquid ammonia. M. S. KHARASCH, E. STERNFELD, and F. R. MAYO (J. Amer. Chem. Soc., 1939, 61, 215).—Addition of EtOBz to 2 Na in liquid NH_3 and evaporation gives a powder (I), which inflames F^* (A., II.)

spontaneously in air, with H_2O gives PhCHO and $\text{CH}_2\text{Ph}\cdot\text{COPh}$, with EtBr gives COPhEt , with BuBr gives COPhBu , and with CH_2PhCl gives $\text{CH}_2\text{Ph}\cdot\text{COPh}$. $(\text{CPh}\cdot\text{ONa})_2$ and NaOEt in liquid NH_3 give (I). $\text{Pr}^\beta\text{CO}_2\text{Et}$ and $\text{Bu}^\gamma\text{CO}_2\text{Et}$ react similarly. The following reactions are postulated. $\text{RCO}_2\text{Et} + \text{Na} \rightarrow \text{OEt}\cdot\text{CR}\cdot\text{ONa}$ (II) $\rightleftharpoons (\text{OEt}\cdot\text{CR}\cdot\text{ONa})_2$ (III) $\rightleftharpoons (\text{COR})_2$ (IV) $\xrightarrow{2\text{Na}}$ $\text{OEt}\cdot\text{CRNa}\cdot\text{ONa}$ (V) [e.g., (I) \rightleftharpoons (III); (IV) + 2 $\text{Na} \rightarrow$ (V); (II) + 2 $\text{Na} \rightarrow$ (V)].

R. S. C.

Constitution of nephromopsic acid. II. M. ASANO and T. AZUMI (Ber., 1939, 72, [B], 35—39).—Treatment of nephromopsic acid (I) with 2 equivs. of KOH and of the solution with AgNO_3 gives a *Ag* salt, transformed by MeI into *Me* nephromopsate (II), identical with that from (I) and CH_3N_3 . Hydrolysis of (II) with $\text{KOH}\cdot\text{EtOH}$ affords dihydro-*l*-protolich-esteric acid, m.p. 103—105°, $[\alpha]_D^{25}$ —33.3° in CHCl_3 , the change involving the racemisation of C_{20} . (I) is unchanged by $\text{KOH}\cdot\text{EtOH}$ at 100°. *Et pelargonoyl-acetate*, b.p. 115°/2 mm., 149—151°/16 mm., from NH_3 and *Et pelargonoylacetoacetate* or from *Et pelargonate*, EtOAc , and Na , is converted by $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ and Na in EtOH at 120° into *Et* α -pelargonoyl- α -methylsuccinate, b.p. 158—162°/3 mm., reduced ($\text{Na}\cdot\text{Hg}$) to α -methyl- γ -octylparaconic acid (II), m.p. 112—114°, and a mixture of esters hydrolysed to (II) and γ -keto- α -methyl-lauric acid, m.p. 62—63° (semicarbazone, m.p. 125—126.5°). The *Et* ester of (II) is transformed by $\text{NaOEt}\cdot\text{EtOH}$ at 90—100° and subsequent hydrolysis into α -methyl- α' -nonylidene-succinic acid, m.p. 132—134°, which with $\text{Br}\cdot\text{H}_2\text{O}$ gives small amounts of an unidentified compound, m.p. 115—120°. *Et* myristoylacetate, $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$, and NaOEt give *Et* α -myristoyl- α -methylsuccinate, reduced and hydrolysed to myristic acid, lichesterylic acid, m.p. 80—83°, and α -methyl- γ -tridecylparaconic acid, m.p. 134—136°. 3-Pelargonoyl-6-octylpyronone, m.p. 70—71°, and 3-myristoyl-6-tridecylpyronone, m.p. 85.5—87° [transformed by HI (*d* 1.7) at 160—170° into *tridecylpyrone*, m.p. 65—66°], are incidentally described. H. W.

X-Ray and thermal examination of the glycerides. IV. Symmetrical mixed triglycerides $\text{CH}(\text{O}\cdot\text{COR}')(\text{CH}_2\text{O}\cdot\text{COR})_2$. T. MALKIN and M. L. MEARA (J.C.S., 1939, 103—108).—The symmetrical mixed triglycerides $\text{CH}(\text{O}\cdot\text{COR}')(\text{CH}_2\text{O}\cdot\text{COR})_2$ are divided into two groups: (a) in which R' is shorter than R , viz., β -decodilaurin (I), β -laurodistearin (II), β -myristodipalmitin (III), β -palmitodistearin (IV), and (b) in which R' is longer than R , viz., β -lauro-didecain (V) (from $\alpha\alpha'$ -didecain and lauroyl chloride), β -myristodilaurin (VI), β -palmitodimyristin (VII), and β -stearodipalmitin (VIII). All the glycerides exist in four solid modifications, vitreous, α , β , and β' , the m.p. of which are, in the order given; (I), 8°, 23°, 33°, 38.5°, (II) 24°, 35°, 45°, 50°, (III) 37°, 46°, 55°, 60°, (IV) 50°, 56°, 64°, 68°, (V) 6°, 25°, 34°, 37.5°, (VI) 24°, 37°, 44°, 48°, (VII) 38°, 49°, 55°, 58.5°, (VIII) 49°, 59°, 65°, 68°. The transition from forms of lower to those of higher m.p. is more rapid than with the simple triglycerides. X-Ray data of the various forms (except vitreous) are given, and support the "tuning fork" structure advanced for the simple

triglycerides (A., 1934, 720). The X-ray spectra of the stable forms of group (a) are different from those of group (b). J. D. R.

Thermal polymerisation of ethyl elæostearate and ethyl $\theta\kappa$ - and $\theta\lambda$ -linoleate. J. S. BROD, W. G. FRANCE, and W. L. EVANS (Ind. Eng. Chem., 1939, 31, 114—118).—Et elæostearate (I) (from tung oil) and mixed Et linoleates (II) (from dehydrated castor oil) are heated at 300°. (I) turns deep yellow in 10 min., whereas (II) becomes yellow only after 12 hr.; a control of Et oleate shows no apparent change. Vals. of mol. wt., η , and diene, acid, and I vals. are observed at intervals. Unpolymerised material is separated from polymerised by high-vac. distillation. With (I), both isomerisation (probably to a cyclic form) and polymerisation (only to the dimeride) occur rapidly; equilibrium is reached at 27% of mono-[isomeric form of (I)] and 73% of di-meride. On further heating, some change in the monomeride continues until no conjugated double linkings are present. Gelation occurs in the triglycerides of the higher unsaturated fatty acids before the max. possible no. of dibasic acids have been formed by intermol. attachment at the double linkings. Since no particles are detected on ultra-microscopic examination of the polymerides in EtOH, no high polymerides or colloidal aggregates are formed. In the case of (II), the $\theta\lambda$ -derivative (III) probably isomerises to the $\theta\kappa$ -derivative, followed by mainly dimerisation of the latter. An apparent equilibrium is reached after about 5 hr. at 300°, corresponding with 2 mols. of mono- [mainly (III)] to 3 mols. of di-meride. Both dimerides, from (I) or (II), probably contain a 6-membered ring. A. T. P.

Ethyl trimesate as by-product of the electrolysis of ethyl hydrogen succinate. F. FICHTER and A. MARITZ (Helv. Chim. Acta, 1939, 22, 265—267).—Et₃ trimesate, m.p. 134—134.5°, is identified among the by-products of higher b.p. obtained by the electrolysis of CO₂H·CH₂·CH₂·CO₂Et; it appears to be formed by the anodic oxidation of immediately formed OH·CH₂·CH₂·CO₂Et. H. W.

Physico-chemical properties of ascorbic and dehydroascorbic acid. J. C. GHOSH and P. C. RAKSHIT (Biochem. Z., 1938, 299, 394—405).—Vals. for $[\alpha]_D^{25}$ of ascorbic acid (I), dehydroascorbic acid (II), and their Na salts are given. The dissociation of (I) and the reducing properties and reversible reduction by H₂S of (II) are described and the circular dichroism of (I) is measured. Pure (II) is obtained from (I) in presence of a small amount of colloidal Pt by adding somewhat > the calc. amount of H₂O₂. W. McC.

Esters of methanetetra-carboxylic acid. H. J. BACKER and J. Lolkema (Rec. trav. chim., 1939, 58, 23—33).—Esters, C(CO₂R)₄ and C(CO₂Pr ^{β})₃·CO₂R', are prepared from ClCO₂R' and CNa(CO₂R)₃ [from CH(CO₂R)₃ and NaOR or Na in xylene]. The following are described: Pr ^{α} , b.p. 195.5—196°/10 mm.; Pr ^{β} , (I), m.p. 76°, b.p. 176°/12—13 mm.; Bu ^{α} , b.p. 184—185°/1.5 mm.; Bu ^{β} , b.p. 177—178°/3 mm.; sec.-Bu, m.p. 42—43°, b.p. 173—174°/2.5 mm.; (n-C₅H₁₁)₄, b.p. 215—215.5°/2.5 mm.; (iso-C₅H₁₁)₄, b.p. 214—217°/4—5 mm.; (CH₃CH₂)₄, b.p. 184°/2.5

mm.; (n-C₁₀H₂₁)₄, b.p. 240—241°/0.001 mm.; (cyclo-C₆H₁₁)₄, (II), m.p. 110°, b.p. 180—200°/0.0005; Me₂Pr ^{β} , [from CH(CO₂Pr ^{β})₂·CO₂Me], m.p. -5°, b.p. 141°/2.5 mm.; Me Pr ^{β} , b.p. 140—141°/2.5 mm.; Pr ^{β} ·CHMeEt, m.p. 35—36°, b.p. 167—168°/5 mm.; cyclo-C₆H₁₁ Pr ^{β} , b.p. 172—173°/2.5 mm.; Ph Pr ^{β} , (III), m.p. 73.5—74°; p-C₆H₄Me Pr ^{β} , m.p. 62—63°. With C(CO₂Et)₄, CO(NH₂)₂ and NaOEt give barbituric acid, whilst NH₂Ph gives CH₂(CO·NHPh)₂ and CO(NHPh)₂. Crystallographic data for (I), (II), and (III) are recorded. E. W. W.

Stepwise degradation of lycopene. P. KÄRER and W. JAFFÉ (Helv. Chim. Acta, 1939, 22, 69—71).—Oxidation of lycopene in C₆H₆ by aq. KMnO₄·Na₂CO₃ and chromatographic purification [Ca(OH)₂] of the product yields bixindialdehyde, m.p. 218° (dioxime, m.p. >250°), apo-1-bixindialdehyde, m.p. 168° (dioxime, sinters >210°), apo-2-lycopenal, m.p. 147° after softening at 144°, and apo-3-lycopenal, m.p. 138°. H. W.

Synthesis of long-chain ketones. J. W. H. OLDHAM and A. R. ÜBBELÖHDE (J.C.S., 1939, 201—202).—Various methods of synthesis of long-chain ketones are reviewed, with respect to yield, convenience, and ease of purification of the product. In the pyrogenetic synthesis by passing the vapours of the two acids over ThO₂, a large excess (10 : 1) of the short-chain acid is used. In the acetoacetic ester synthesis, the acyl derivative is first prepared and then treated with an alkyl halide, which should be <4 C. Interaction of long-chain nitriles with a short-chain Grignard reagent is recommended in certain cases, particularly for the synthesis of diketones. J. D. R.

Crystalline D-altrosan. N. K. RICHTMYER and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 214—215).—D-Altrosan, m.p. 80—90°, $[\alpha]_D^{20}$ -215° in H₂O, is obtained from D-altrose and hot HCl (cf. A., 1935, 1355) and with N-HCl gives the known altrose equilibrium mixture. R. S. C.

Preparation of rhamnose from naringin. G. N. PULLEY and H. W. VON LOESECKE (J. Amer. Chem. Soc., 1939, 61, 175—176).—Prep. of rhamnose from naringin (obtained from grapefruit cannery waste) is detailed. R. S. C.

Synthetic sugar anhydrides. IX. Further anhydride from 2 : 3 : 6-trimethylglucose. K. HESS and K. E. HEUMANN (Ber., 1939, 72, [B], 137—148).—2 : 3 : 6-Trimethylglucofuranose 1-acetate 5-p-toluenesulphonate is converted by NaOEt into a trimethylhexose anhydride (I), b.p. 34—35°/0.0008 mm., m.p. 8.7°, $[\alpha]_D^{20}$ -1.8° in H₂O, -1.6° in MeOH, -0.8° in CHCl₃, +2.84° (in substance), which is stable towards boiling Fehling's solution, is hydrolysed by 20% HCl to a reducing sugar, is not immediately affected by Na₂CO₃·KMnO₄, does not decolorise Br in CHCl₃, is unaffected by Na, and remains unchanged at 100—105° in a sealed tube. Its non-identity with idose anhydride and considerations of space models cause (I) to be regarded as a glucose derivative. (I) is very resistant towards acid hydrolysis and the reducing product (II) obtained from it with boiling 20% HCl is not identical with trimethyl-l-idose or trimethyl-d-glucose. Treatment

of (I) with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ followed by hydrolysis of the acetate gives a hexose with different sp. rotation ($[\alpha]_D^{20} +9.4^\circ$) but similar composition so that Walden inversion appears to occur during hydrolysis either at $\text{C}_{(4)}$ or $\text{C}_{(5)}$ or simultaneously at $\text{C}_{(4)}$ and $\text{C}_{(5)}$ according to the nature of the reagent. Demethylation of (II) by HBr leads to elimination of only 2 Me groups whilst the use of more drastic conditions leads to humification. H. W.

Sterically homogeneous forms of 2:3:6-trimethylmethyl- β -D-glucofuranoside and its derivatives. K. HESS and K. E. HEUMANN (Ber., 1939, 72, [B], 149—158).—During glucosidification of 2:3:6-trimethylglucose by 1% $\text{HCl}-\text{MeOH}$ at 20° , $[\alpha]_D^{20}$ of the product passes through a min. after 20 hr. The mixture thus obtained is separated by fractional distillation of its compound with CaCl_2 (under defined conditions) into greatly enriched samples of the α - (I) and β - (II) -forms of 2:3:6-trimethylmethyl- β -D-glucofuranoside. (II) is transformed by $p\text{-C}_6\text{H}_4\text{Me}-\text{SO}_2\text{Cl}$ in $\text{C}_6\text{H}_5\text{N}$ into 2:3:6-trimethyl- β -methyl- β -D-glucofuranoside 5- p -toluenesulphonate (III), m.p. $51-52^\circ$, $[\alpha]_D^{20} -62.1^\circ$ in MeOH , -60.4° in C_6H_6 , -57.7° in CHCl_3 , reduced ($\text{Na}-\text{Hg}$) to homogeneous, non-cryst. (III), b.p. $70-72^\circ/0.005\text{ mm.}$, $[\alpha]_D^{20} -97.5^\circ$ in MeOH , -91.6° in CHCl_3 , -88.0° in H_2O , re-converted into (II). TiCl_4 in CHCl_3 isomerises (III) to 2:3:6-trimethyl- α -methyl- β -D-glucofuranoside 5- p -toluenesulphonate (IV), a syrup, $[\alpha]_D^{20} +97.7^\circ$ in MeOH , $+92.6^\circ$ in CHCl_3 , $+95.9^\circ$ in C_6H_6 , reduced to 2:3:6-trimethyl-2-methyl- β -D-glucofuranoside, $[\alpha]_D^{20} +95.7^\circ$ in MeOH , $+91.6^\circ$ in CHCl_3 , $+88.7^\circ$ in H_2O . (VI) is methylated ($\text{Ag}_2\text{O}-\text{MeI}$) to 2:3:5:6-tetramethyl- β -methyl- β -D-glucofuranose, b.p. $48-50^\circ/0.003\text{ mm.}$, $[\alpha]_D^{20} -74.1^\circ$ in CHCl_3 , -72.7° in MeOH , -67.3° in H_2O , hydrolysed by 2% HCl to 2:3:5:6-tetramethyl- β -D-glucofuranose, $[\alpha]_D^{20} -24.8^\circ$ in CHCl_3 . BzCl in $\text{CHCl}_3-\text{C}_6\text{H}_5\text{N}$ transforms (II) at 40° into 2:3:6-trimethyl- β -methyl- β -D-glucofuranoside 5-benzoate, m.p. $55-56^\circ$, $[\alpha]_D^{20} -92.6^\circ$ in CHCl_3 , -104.2° in MeOH , -138.0° in C_6H_6 , converted by $\text{HCl}-\text{Et}_2\text{O}$ into homogeneous, cryst. 1-chloro-2:3:6-trimethyl- β -D-glucofuranose 5-benzoate and isomerised by TiCl_4 into 2:3:6-trimethyl- α -methyl- β -D-glucofuranoside 5-benzoate, a colourless syrup, $[\alpha]_D^{20} +54.4^\circ$ in MeOH , $+53.5^\circ$ in CHCl_3 , $+46.5^\circ$ in C_6H_6 . Under varied conditions (III) is transformed by $\text{HCl}-\text{Ac}_2\text{O}$, $\text{HCl}-\text{Et}_2\text{O}$, or liquid HCl into a non-cryst. mixture of 1-chloro-2:3:6-trimethyl- α - β -D-glucofuranose p -toluenesulphonates, $[\alpha]_D^{20} +15.5^\circ$ in CHCl_3 . A mixture of 2:3:6-trimethyl- β -D-glucofuranose 1-acetate 2- p -toluenesulphonates is derived from (III) or (IV) and $\text{H}_2\text{SO}_4-\text{Ac}_2\text{O}$. H. W.

Transformation of α - and β -forms of 3:6-anhydromethylgalactosides. W. N. HAWORTH, J. JACKSON, and F. SMITH (Nature, 1938, 142, 1075—1076).—Liquid 2:4-dimethyl-3:6-anhydro- α -methyl- β -D-galactopyranoside (prep. given) changes to the corresponding cryst. β -form on brief contact with air containing a trace of HCl . Ebullioscopic methods, and X-ray examination of the β -form, indicate that both forms are monomeric. The same change can be effected by addition of a drop of a solution of HCl in EtOH or Et_2O . Hydrolysis to the free sugar,

followed by mutarotation, and regeneration of the two forms of the methylglucoside, does not apply to this case. L. S. T.

Action of mercury salts on acetohalogeno-sugars. XII. Advantageous synthesis of primverose derivatives and of primverose. G. ZEMPLÉN and R. BOGNÁR (Ber., 1939, 72, [B], 47—49; cf. A., 1938, II, 219).— α -Acetobromoxylose, α -1-chloroglucose 2:3:4-triacetate, and $\text{Hg}(\text{OAc})_2$ in C_6H_6 at $40-50^\circ$ give acetochloroprimverose (I), m.p. $190-192^\circ$ after incipient decomp. at 186° , $[\alpha]_D^{20} +70.8^\circ$ in CHCl_3 , in 50.7% yield. AgOAc in Ac_2O at 100° converts (I) into a mixture (mainly β) of primverose hepta-acetates, hydrolysed to primverose and converted by TiBr_4 in CHCl_3 free from EtOH into cryst. α -acetobromoprimverose, $[\alpha]_D^{20} +122.6^\circ$ in CHCl_3 . H. W.

Emulsin. XXXVI. Enzymic fission of lactose, lactulose, and neolactose. B. HELFERICH and W. W. PIOMAN (Ber., 1939, 72, [B], 212—215).—In accordance with the β -D-galactosidatic action of emulsin of sweet almonds, lactose, lactulose (I), and neolactose (II) are qualitatively hydrolysed by the enzyme. With all three substrates the activity increases markedly when the enzyme purified by Ag pptn. is substituted for the crude enzyme. Since this mode of purification causes almost complete removal of α -D-galactosidase this increase in the rate of hydrolysis of (I) and (II) is proof of the retention of the β -configuration of galactose in (I) and (II). H. W.

Synthesis of a new glucogallic acid. F. MAUTHNER (J. pr. Chem., 1939, [ii], 152, 20—23).—Addition of Ag_2O to 3:4:5:1-($\text{OMe})_2\text{C}_6\text{H}_2(\text{OH})\text{CO}_2\text{Me}$ and acetobromoglucose in anhyd. quinoline followed by hydrolysis of the product gives 3:4-dimethoxy-5-glucosoxybenzoic acid, m.p. $197-198^\circ$. H. W.

Action of amylases on substances of low mol. wt. K. MYRBÄCK and B. ÖRTENBLAD (Svensk Kem. Tidskr., 1938, 50, 284—297).—Experiments with native starches and the degradation products obtained therefrom by heating in glycerol, by treatment with cold conc. HCl , or by enzymes show that β -amylase gives about 60% of maltose (I) from starch and dextrans of mol. wt. comparable with that of the parent. Apparently various starch mols. are saccharified in very varying degree, some probably completely to (I), others little or not at all. The cause must lie in anomalies in structure. The enzyme removes a mol. of (I) from the non-reducing end of the chain and the process continues until the first anomaly is reached, when fission ceases. It is impossible to assume that the substitution by PO_4 etc. plays an exclusive part or that fission ceases at a definite chain length since the β -dextrans are highly non-uniform. Malt α -amylase (II) hydrolyses starch primarily to dextrans which are not coloured by I. In the case of potato starch these have a mean mol. wt. of about 7000 (= about 45 glucose residues). Little (I) is formed during this dextrinisation but the viscosity diminishes greatly so that it is doubtful if the enzyme is actually "disaggregating." The products of the action show

a well-defined reduction, showing that glucose unions are disrupted. Starch therefore appears to contain linkings other than the normal (I) unions to some extent and these are broken by (II). The action of the enzyme does not proceed from the ends of the chains. It appears that (II) hydrolyses well-defined linkings. These are not necessarily β -glucosidic but may be α -glucosidic 1:6 or 1:3 unions or 1:4 linkings between glucose residues which are abnormal in some manner. Natural mixtures of α - and β -enzymes and certain amylases (taka-diaxase, animal amylases) which are considered to be uniform α -compounds hydrolyse starch with production of much (I) (yield often >90%). The limit dextrins have a low mol. wt., the chain length being frequently only 4—6 glucose units. The experiments are difficult to evaluate since little is known of the enzymic uniformity of the preps. The great variations in the yield of (I) show that natural amylases in addition to the normal amylases contain substances which influence the degree of saccharification. It is considered that these substances attack linkings which are immune to the normal material and hence can hydrolyse certain limit dextrins. Hydrolysis of native starches by amylase appears to establish the existence in starch of linkings other than the customary maltose unions. The no. of these linkings is probably relatively small and the anomalies may be accumulated in the limit dextrins. The results are fully confirmed by observations with the degraded products of starch.

H. W.

Cellulose compounds. E. BERL and W. KOEHLER (J. Amer. Chem. Soc., 1939, 61, 154—157).—The microscopic appearance of cellulose nitrates (12.02—13.9% N) in Et_2O , EtOH , $\text{Et}_2\text{O}-\text{EtOH}$ (3:2), MeOH , AcOH , $(\text{CH}_2\text{OH})_2$, Ac_2O , HCO_2H , EtOAc , and MeOAc is recorded. Some of the nitrates are more sol. in $\text{Et}_2\text{O}-\text{EtOH}$, MeOH , and MeOAc at -50° than at 0° , indicating formation of mol. compounds which dissociate at 0° .

R. S. C.

Oxycellulose. I. II. **New reaction of hydro-cellulose.** F. MÜLLER (Helv. Chim. Acta, 1939, 22, 208—216, 217—224).—I. Oxidised cellulose adds $\text{Na}_2\text{S}_2\text{O}_4$ and thereby gains a marked increase in the reducing power proper to this compound. All methods of detecting oxycellulose (I) which depend on its reducing action are influenced by this pretreatment, the effect being most marked with Haller's gold-purple reaction. All these methods are trustworthy only in the absence of reducing impurities of non-cellulosic nature. Hydrocellulose (II) does not add $\text{Na}_2\text{S}_2\text{O}_4$. Witz's reaction with $\text{NHPh}\cdot\text{NH}_2$ for (I) has been extended in such a manner that it becomes more sp. than any other method since it depends on the presence of CO in the oxidised product. For this purpose diazo-components (from *p*- or *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; naphthionic or Cleve acid; *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$) are coupled with arylhydrazones formed by the action of arylhydrazines or (I); azo-dyes are formed at the points of oxidative attack. Certain aromatic hydrazines (hydrazinonaphthalene- and hydrazinonaphthol-sulphonic acids and the corresponding derivatives of Ph_2) react with (I) but not with (II).

II. Reaction occurs between (II) and certain

derivatives of $\text{NHPh}\cdot\text{NH}_2$, particularly the *p*-sulphonic acids. For its detection "true-blue salt B" and "variamine-blue salt F.G." are the sole suitable diazo-components. All the reactions of (I) establish the existence of small amounts of true oxidation products with CO groups. Primarily CO is not present in (II); this conception is in harmony with Hess' formulation of the reaction complex as cellulose-A.

H. W.

Preparation and properties of ethyldideuteramine and dimethyldideuteramine. E. R. ROBERTS, H. J. EMELÉUS, and H. V. A. BRISCOE (J.C.S., 1939, 41—52).—Three successive treatments of $\text{NH}_2\text{Et}\cdot\text{HCl}$ with D_2O , each followed by evaporation of the aq. D_2O , and final liberation of the base with CaO yield ethyldideuteramine (I), b.p. $17.4-17.5^\circ$, m.p. -78.5° . Similar treatment of $\text{NHMe}_2\cdot\text{HCl}$ yields dimethyldideuteramine (II), b.p. $6.9-6.94^\circ$, m.p. -93° . The v.p. curves and ultra-violet absorption spectra of (I) and (II) are recorded, and a method of determination of their v.d. is described in which the amine and deuteramine are brought to the same density and the pressure difference is measured on a new type of differential gauge. Treatment of $\text{NH}_2\text{Et}\cdot\text{HCl}$ with a large excess of D_2O , or of $\text{NMe}_3\cdot\text{HCl}$ with D_2O , or circulation of $\text{NH}_2\text{Me}-\text{D}_2\text{O}$ or $\text{ND}_2\text{Me}-\text{D}_2\text{O}$ mixtures over a reduced Ni catalyst at $20-195^\circ$ gives no evidence of replacement of H by D in the alkyl groups.

J. D. R.

Photolysis of organic nitrogen compounds. I. Dimethyl- and diethyl-nitrosoamines. II. Aliphatic amines. C. H. BAMFORD (J.C.S., 1939, 12—17, 17—26).—I. Irradiation of $\text{NMe}_2\cdot\text{NO}$ and $\text{NEt}_2\cdot\text{NO}$ by light of all λ lying in the absorption band causes decomp. to the sec. amine, NO, N_2 , H_2 , and olefines, the quantum yield of NO in all cases being small. The vapours exhibit no fluorescence. The primary dissociation is $\text{NR}_2\cdot\text{NO} \rightarrow \text{NR}_2\cdot + \text{NO}$, the energy for this change being estimated at 12 kg.-cal. The NR_2 radical then undergoes a disproportionation reaction to NHR_2 and a bivalent radical which subsequently polymerises. Prolonged irradiation produces H_2 by photolysis of NHR_2 . Other possible secondary reactions producing N_2 and olefines are suggested and the nature of the primary dissociation is discussed in relation to the absorption spectra of the nitrosoamines and the photolysis of other NO-compounds.

II. Irradiation of NHMe_2 , NH_2Bu^n , $\text{C}_2\text{H}_{11}\cdot\text{NH}_2$, and NMe_3 in the vapour phase by the full light of the Hg arc causes decomp. From primary and sec. amines, the primary dissociation process produces H atoms and alkylamino- or dialkylamino-radicals, respectively. Dialkylamino-radicals then undergo exclusively disproportionation to sec. amine and a bivalent radical which polymerises. Alkylamino-radicals are partly disproportioned to primary amine and an unsaturated radical which polymerises, and partly converted into a Schiff's base and NH_3 . *tert*-Amines first split off alkyl, the remaining dialkylamino-radicals reacting as above. Irradiation of NHMe_2 and NH_2Et in presence of NO gives no nitrosoamine, but irradiation of NMe_3 and NO gives HCN, probably from reaction between Me and NO.

J. D. R.

Preparation and configurative relationships of methylglucosaminides. A. NEUBERGER and R. P. RIVERS (J.C.S., 1939, 122—126).—*N*-Carbobenzyl-oxyglucosamine (I) in MeOH with HCl at 40° yields *N*-carbobenzyl-oxy- α -methylglucosaminide, m.p. 154—155°, $[\alpha]_D +80^\circ$ in C_5H_5N , reduced (Pd-H₂ in EtOH-HCl) to α -methylglucosaminide hydrochloride (II), m.p. 119°, $[\alpha]_D +127^\circ$ in H₂O, which by treatment with keten after neutralisation with Ag₂O yields *N*-acetyl-methylglucosaminide. When the above glycoside synthesis with (I) is carried out at room temp., *N*-carbobenzyl-oxy- β -methylglucosaminide, m.p. 166—168°, $[\alpha]_D -38^\circ$ in C_5H_5N , is formed, reduced to (II), which after neutralisation (Ag₂O) yields with keten, *N*-acetyl- α -methylglucosaminide, m.p. 195—196°, $[\alpha]_D -43^\circ$ in H₂O. Tetra-acetylglucosamine hydrochloride in aq. NaHCO₃ with ClCO₂CH₂Ph at 0° yields *N*-carbobenzyl-oxytetra-acetylglucosamine, m.p. 150—151°, $[\alpha]_D +21.5^\circ$ in C_5H_5N , also formed by acetylation of (I). Comparison of the rates of hydrolysis of the two glucosaminides shows that the α -form has the *cis* configuration at C₁. It is shown that Hudson's two rules of optical superposition are closely obeyed, and it is deduced that glucosamine has the same structure as glucose. J. D. R.

"Methylepiglucosamine" and 2-amino- α -methylaltroside. G. J. ROBERTSON, W. H. MYERS, and W. E. TETLOW (Nature, 1938, 142, 1076—1077).—Cryst. derivatives of idose can be obtained from galactose derivatives by using an anhydro-compound of the (CH₂)₂O type in which the ring is broken by means of alkali. With NH₃, 2:3-anhydro-4:6-benzylidene- α -methylmannoside gives a quant. yield of 3-amino-4:6-benzylidene- α -methylaltroside, m.p. 188°, $[\alpha]_D +88.9^\circ$ in CHCl₃, which with 1% HCl yields (76%) 3-amino- α -methylaltroside hydrochloride, m.p. 209° (decomp.), $[\alpha]_D -149^\circ$ in H₂O, identical with the "methylepiglucosamine hydrochloride" of Fischer *et al.* Similarly, 2:3-anhydro-4:6-benzylidene- α -methylaltroside gives a quant. yield of 2-amino-4:6-benzylidene- α -methylaltroside, m.p. 168°, $[\alpha]_D +104.7^\circ$ in CHCl₃, which in turn yields (70%) 2-amino- α -methylaltroside, m.p. 193°, $[\alpha]_D +107^\circ$ in CHCl₃. L. S. T.

New form of stereoisomerism and a new form of glycine. Theoretical interpretation. R. ENGELAND (Compt. rend., 1938, 207, 1211—1213).—From the hydrolytic product of elastin a Cu salt of glycine, which is different in colour and cryst. form from the known salt, and loses its H₂O of hydration at 100°, is isolated. An aq. solution of the new salt when seeded with the known salt is transformed into the latter; the reverse change does not occur. The isomerism is explained by postulating the existence of the H of CH₂ in "ortho-" and "para-" positions, the two possible "ortho-" forms being unstable and the "para-" forms stable and identical thermodynamically. A similar hypothesis serves to explain the existence of several optical isomerides in certain cases, of two different optically inactive betaines of γ -amino- β -hydroxybutyric acid, of > two forms of substances of the cinnamic acid type, and of polymorphism in the fatty acids. J. L. D.

Polymeric anhydrides of glycine and asparagine. K. FREUDENBERG, G. PIAZOLO, and C.

KNOEVENAGEL (Annalen, 1939, 537, 197—204).—20N-H₂SO₄ converts polymeric glycine anhydride into a substance, which from its NH₂ content is a hepta- or octa-peptide; in agreement with this (cf. Kuhn *et al.*, A., 1932, 935), *k* for hydrolysis of the product is 0.0035—0.0036. Azidosuccinic acid, m.p. 95°, is converted by hot SOCl₂ into the anhydride (I), b.p. 95—96°/0.3 mm. NH₂Ph and (I) give azidosuccinimonoanilide, m.p. 91°, reduced by H₂-Pd-black in Et₂O to asparagineanilide, m.p. ~120° (decomp.). H₂-Pd reduces (I) in dioxan to polymeric asparagine anhydride. R. S. C.

Preparation of α -amino-acids through α -oximino-esters. H. McILWAIN and G. M. RICHARDSON (Biochem. J., 1939, 33, 44—46).—Et₂ α -acetylglutarate, prepared by a modification of the method of Clemons and Welch (A., 1928, 1252), is converted into the oximinoglutamate (I) by that of Wislicenus and Grützner (A., 1909, i, 477). (I) in AcOH is reduced (PtO₂-H₂ and Na₂SO₄ for 3 days) to the NH₂-ester, hydrolysed with boiling 5N-HCl to glutamic acid hydrochloride. The free acid is obtained by adding NH₂Ph and EtOH to the aq. solution of the hydrochloride and heating. The overall yield is 39%. δ -Chloro- α -acetyl- γ -valerolactone in cooled H₂SO₄ and NO-SO₄H in H₂SO₄ give 67% of δ -chloro- α -oximino- γ -valerolactone, m.p. 118°, reduced to the corresponding NH₂-compound [acetate (II), m.p. 177°; hydrochloride] by PtO₂-H₂. (II) and saturated aq. NH₃ at 30° give hydroxyproline in yield inferior to that obtained by Leuchs (A., 1905, i, 545). Et α -oximinoacetate reduced and hydrolysed (Harrington and Randal, A., 1932, 257) gives only NH₂-CHET-CO₂H (III) in 80% yield: with Pd-C, HCl in EtOH, and H₂ it gives 62% of Et α -amino- β -ketobutyrate (IV), m.p. 125°. Further reduction of (IV) gives (III) or Et₂ 2:5-dimethylpyrazine-3:6-dicarboxylate. W. McC.

Chemistry of the reaction of creatinine with 3:5-dinitrobenzoic acid. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1938, 71, 223—229; cf. A., 1936, 1397).—Treatment of creatinine (I) with 3:5-(NO₂)₂C₆H₃-CO₂H (II) and NaOH in EtOH gives dark purple, cryst. ppts. containing (I) and (II) in the mol. ratio 1:2 and varying amounts of NaOH or Na depending largely on the amounts of NaOH added. They exist also in more stable, brown forms. Under defined conditions a compound, $\{[(NO_2)_2C_6H_3-CO_2H]_2C_4H_7ON_3\} \cdot 3NaOH \cdot 3H_2O$, is obtained, transformed by AgNO₃ into the substance, $\{[(NO_2)_2C_6H_3-CO_2H]_2C_4H_7ON_3\} \cdot 3Ag$ and decomposed by MeOH into (NO₂)₂C₆H₃-CO₂Na, (I), and the compound, $\{[(NO_2)_2C_6H_3-CO_2H]_2C_4H_7ON_3\} \cdot 4NaOH \cdot 4H_2O$, whence (AgNO₃) the substance, $\{[(NO_2)_2C_6H_3-CO_2H]_2C_4H_7ON_3\} \cdot 4AgOH$. H. W.

Sulphoxide of methionine. G. TOENNIES (Science, 1938, 88, 545—546).—dl-Methionine perchlorate in Pr^oOH with an excess of H₂O₂ consumes 1 O per mol. Neutralisation with C₅H₁₁NH₂ ppts. pure methionine sulphoxide (I) (yield >90%). The amorphous ppt. is converted into microcryst. aggregates, decomp. 220—230°, by pptn. by COMe₂ from H₂O or aq. MeOH. L. S. T.

Preparation of methyleneaminoacetonitrile. L. H. AMUNDSEN and R. VELITZKIN (J. Amer. Chem. Soc., 1939, **61**, 212).—The yield is improved to 45–55%. R. S. C.

Nucleic acids. XII. Thymic acid. H. BREDERECK and G. MÜLLER (Ber., 1939, **72**, [B], 115–121; cf. Feulgen, A., 1918, *i*, 413).—Thymic acid (I), obtained by the hydrolysis of thymonucleic acid with NaHSO_4 , is shown by the HCl-MeOH test to be free from guanine and adenine. Contrary to Feulgen, (I) is very stable in H_2O and becomes scarcely coloured when the aq. solution is evaporated at room temp. in a vac. At increased temp. it darkens rapidly. In neutral and, particularly, in alkaline solution there is a gradual formation of acid which is probably caused by fission into nucleotides (II) or deoxyribosephosphoric acid (III). (I) is completely hydrolysed by an enzyme prep. from sweet almonds, 100% PO_4 fission corresponding with an increase in acidity of about 3 equivs. Since a substrate solution + buffer alone does not show any change, this increase in acidity is due essentially to fission of (I) into (II) and (III) from which H_3PO_4 is eliminated in a secondary change by nucleotidase without involving an increase in the acidity towards phenolphthalein. Direct titration and determination of the increase in acidity during fermentative hydrolysis show that (I) is pentabasic and hence that Feulgen's formulation cannot be correct. (I) is considered to be phosphoric acid (IV)-deoxyribose (V)-(IV)-(V) (thymine)-(IV)-(V) (cytosine)-(IV)-(V). H. W.

Nucleic acids. XIII. Constitution of polynucleotides; basicity of thymonucleic acid. H. BREDERECK and M. KÖTHNIG (Ber., 1939, **72**, [B], 121–126).—It is shown by direct titration and by determination of the increase in acidity during enzymic fission that thymonucleic acid is pentabasic. The constitution $(\text{OH})_2\text{PO}[\text{O} \cdot \text{R} \cdot \text{O} \cdot \text{PO}(\text{OH})_2]_3 \cdot \text{O} \cdot \text{R}$, where R = sugar base, therefore appears assured. H. W.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative electronegativities of organic radicals. M. S. KHARASCH and S. SWARTZ (J. Org. Chem., 1938, **3**, 405–408).—When *Hg benzyl allyl* (I) is treated with HCl one half of the Hg is recovered as $\text{CH}_2\text{Ph} \cdot \text{HgCl}$ but the state of the remainder is undisclosed except that it is in part inorg. *Hg Ph allyl* and HCl give HgPhCl in about 50% yield; the remainder is HgCl formed with $\text{CHMe} \cdot \text{CH}_2$ by the action of HCl on Hg allyl chloride . The possible explanation that Ph and allyl have the same electronegativity is rejected in favour of the hypothesis, $\text{HgPh} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 + \text{H}^+ + \text{Cl}^- \rightarrow$

$\text{HgPh} \cdot \text{CH}_2 \cdot \text{CH} + \text{Cl} \rightarrow \text{CHMe} \cdot \text{CH}_2 + \text{HgPhCl}$. The explanation is applied also in the case of (I). In petroleum, $\text{HgPh} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$ is transformed by HCl in C_6H_6 by I or HCl into the HgPh halide in ~50% yield. Only in the first case is there any evidence of the production of Hg allyl iodide . Cleavage with HCl of unsymmetrical organomercuric compounds of the type $\text{R} \cdot \text{Hg} \cdot \text{allyl}$ is not a valid method for comparing the electronegativities of the radicals

in question. *Hg Bu' chloride* sublimes at 131° when placed in a preheated bath. H. W.

Interpretation of secondary reactions observed in the condensation of aliphatic ketones and esters with organomagnesium compounds. Theoretical. M. TUOT (Compt. rend., 1938, **207**, 1227–1230; cf. A., 1938, II, 257, 260).—In the interaction of ketones with Mg org. compounds, the formation of ketone, ketol, and sec. alcohol with the liberation of saturated and unsaturated hydrocarbons always occurs but the extent of the enolisation or reduction reaction depends on the mol. wt. of the ketone. The smaller is the mol. wt. the greater is the enolisation reaction. These reactions are explained on an electronic basis. J. L. D.

Complex metallic salts. VIII, IX.—See A., 1939, I, 61.

Effect of beryllium, magnesium, zinc, and cadmium bromides on the bromination of benzene. R. PAJEAU (Compt. rend., 1938, **207**, 1420–1422; cf. A., 1936, 976).— BeBr_2 , CdBr_2 , and ZnBr_2 catalyse the bromination of dry C_6H_6 at 100° to form PhBr and *p*- $\text{C}_6\text{H}_4\text{Br}_2$, BeBr_2 being the most active. MgBr_2 has a very low activity. J. L. D.

Aromatic nitro-derivatives. XVI. 3:4-Dinitrotoluene: reactivity and nuclear configuration. A. MANGINI and M. COLONNA (Gazzetta, 1938, **68**, 708–718).—The configuration previously proposed (A., 1939, II, 13) is supported. 1:3:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ (I) with $\text{EtOH} \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gives 4-nitro-*m*-tolylhydrazine (II), m.p. $131\text{--}132^\circ$ (*Ac*, m.p. $167.5\text{--}168.5^\circ$, CO_2Et , m.p. $108\text{--}109^\circ$, *CHPh*, m.p. $160\text{--}161^\circ$, and *CMe*, m.p. $84\text{--}84.5^\circ$, derivatives) (oxidised by $\text{CuSO}_4 \cdot \text{AcOH}$ to *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$), and 1-hydroxy-5-methyl-1:2:3-benzotriazole, m.p. 184° (decomp.) (*Bz*, m.p. $129\text{--}130^\circ$, and *Ac* derivative, m.p. $145.5\text{--}146.5^\circ$) (cf. Brady *et al.*, A., 1928, 308). With $\text{NHMe} \cdot \text{NH}_2$, (I) gives α -(4-nitro-*m*-tolyl)- α -methylhydrazine, m.p. $82\text{--}83^\circ$ (*Ac*, m.p. $169\text{--}170^\circ$, and *CHPh* derivative, m.p. $112\text{--}113^\circ$) (oxidised by $\text{CuSO}_4 \cdot \text{AcOH}$ to 4:1:3- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHMe}$). With $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2 \cdot \text{HCl}$ in $\text{EtOH} + \text{NaOAc}$, (I) slowly gives 4-nitro-*m*-tolylsemicarbazide, m.p. $211\text{--}212^\circ$, also obtained from (II) and $\text{KCNO} \cdot \text{HCl}$. E. W. W.

Reactions of paraffins with aromatic hydrocarbons. II. Aromatic hydrocarbons and $\beta\beta$ -trimethylpentane. A. V. GROSSE, J. M. MAVITY, and V. N. IPATIEV (J. Org. Chem., 1938, **3**, 448–455; cf. A., 1939, II, 13).—Destructive alkylation occurs with PhMe or Ph_2 and $\text{CMe}_3 \cdot \text{CH}_2\text{Pr}^6$ (I) in presence of AlCl_3 and HCl giving CHMe_3 and *m*- and *p*- $\text{C}_6\text{H}_4\text{MeBu'}$ or *p*-tert.-butyldiphenyl, m.p. 53.1° (prep. from *p*- $\text{C}_6\text{H}_4\text{Bu'Br}$ and LiPh), respectively. With PhEt and *p*-xylene the alkylation is complicated by migration of Et and Me giving polyethyl- and polymethyl-benzenes. Fluorene and (I) give CHMe_3 and difluorenyl, m.p. $230.2\text{--}230.7^\circ$. With C_{10}H_8 and pyrene alkylation could not be established and substantially all the paraffin could be recovered unchanged. H. W.

Polymethylbenzenes. XXII. Action of aluminium chloride on aromatic hydrocarbons.

I. 1:3-Dimethyl-4-butylbenzenes [4-butyl-*m*-xylenes]. (MISS) D. NIGHTINGALE and L. I. SMITH (J. Amer. Chem. Soc., 1939, 61, 101—104; cf. A., 1938, II, 178).—1:3:4- $C_6H_3Me_2 \cdot COPr^a$, b.p. 118°/8 mm., prepared by a Friedel-Crafts reaction in CS_2 in 53% yield, with Zn-Hg-HCl gives 4-*n*-butyl-*m*-xylene, b.p. 96°/8 mm. [$(NO_2)_3$ -derivative, m.p. 91°], which with $AlCl_3$ at 100° gives 5-sec.-butyl-*m*-xylene, b.p. 98°/15 mm. [$(NO_2)_3$ -derivative, m.p. 97°], also obtained from *m*-xylene, Bu^aCl , and $AlCl_3$ (method: Shoosmith *et al.*, A., 1931, 79). 4-tert.-Butyl-*m*-xylene, m.p. -31°, b.p. 86°/12 mm. [$(NO_2)_3$ -derivative, m.p. 112°] (prep. from *m*-xylene, H_2SO_4 , and Bu^aOH or Bu^aOH at 0° in 41 and 21% yield, respectively), and 4-sec.-butyl-*m*-xylene, b.p. 84°/8 mm. [$(NO_2)_3$ -derivative, m.p. 107°] (from *m*-xylene, $CHMeEt \cdot OH$, and H_2SO_4), with $AlCl_3$ at 100° both give 5-tert.-butyl-*m*-xylene, m.p. -21.5° [$(NO_2)_3$ -derivative, new m.p. 113°] (prep. from *m*-xylene, Bu^aCl , and $AlCl_3$). 4-iso-Butyl-*m*-xylene, b.p. 96°/15 mm., is obtained from 1:3:4- $C_6H_3Me_2 \cdot COPr^b$, b.p. 121°/14 mm. (prep. by a Friedel-Crafts reaction in CS_2 in 72% yield), and with $AlCl_3$ at 100° gives a mixture of hydrocarbons. In the reactions with $AlCl_3$, *m*-xylene and (probably) higher alkylated benzenes are also formed.

R. S. C.

Effect of substitution on the dissociation of hexa-arylethanes. VI. Hexa-*m*-diphenyl-ethane. C. S. MARVEL, E. GINSBERG, and M. B. MUELLER (J. Amer. Chem. Soc., 1939, 61, 77—78; cf. A., 1938, II, 48).—The Grignard reagent from 3-bromodiphenyl (prep. from *m*- $C_6H_4Br \cdot NH_2$ and C_6H_6), b.p. 169—173°/17 mm., and Et_2CO_3 give (*m*- C_6H_4Ph)₃C-OH and thence ($HCl-CaCl_2-Et_2O$) tri-*m*-diphenylmethyl chloride, m.p. 200—201°, which with Ag in C_6H_6 gives $C_2(C_6H_4Ph \cdot m)_6$, which is shown by its χ to be 59—60% dissociated in C_6H_6 (~2.5% solution) at 25°, and gives the peroxide, m.p. 179.5—180°.

R. S. C.

Diarylmethane derivatives. IV. Properties of di- α -naphthylmethyl radical and ion. P. J. WUIS and D. MULDER (Rec. trav. chim., 1938, 57, 1385—1396; cf. A., 1938, II, 89; Schmidlin and Massini, A., 1909, i, 561).— $CHCl(C_{10}H_7 \cdot 1)_2$ (I) and mol. Ag in C_6H_6 (or cyclohexane) in vac. afford primarily di- α -naphthylmethyl, which quickly and completely affords $[CH(C_{10}H_7 \cdot 1)_2]_2O$ (33—39%), $(1-C_{10}H_7)_2CH \cdot OH$ (III) (26—27%), and a syrup (32—33%) are formed. (II) is obtained in CO_2 , which is not absorbed. (II) is stable to NO in C_6H_6 . Conductivities in liquid SO_2 at -10° of (I), (III), the Me (IV), m.p. 138°, and Et ether, m.p. 135—136°, and the acetate (V), m.p. 143—144°, of (III) are recorded. (IV) is obtained from (I) and boiling MeOH and from (V) and MeOH containing 1% HCl (essential). (V) [from (I) and $AgOAc$ in Et_2O or $AcOH$ alone in absence of H_2O] is hydrolysed (MeOH-KOH) to (III). A. T. P.

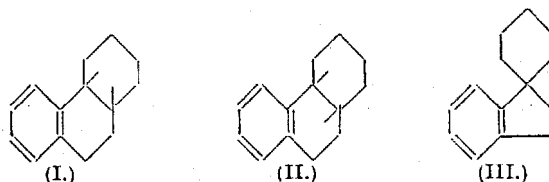
Rôle of peroxides in oxidation of hydrocarbons.—See A., 1939, 1, 149.

Hydrogenation of anthracene and some of the resultant products. H. I. WATERMAN, J. J.

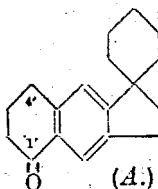
LEENDERTSE, and A. C. CRANEDONK (Rec. trav. chim., 1939, 58, 83—92).—High-pressure hydrogenation (Ni-kieselguhr) of pure anthracene at 180—220° gives first octahydroanthracene, which (using fresh catalyst) further takes up 6 H to give mixed solid (m.p. 88—89°) and liquid products, of composition $C_{14}H_{24}$. The liquid portion after prolonged heating gives more solid, apparently by isomerisation. Both r_i (which is the same for all products) and $[P]$ indicate the presence of 2.8—2.9 rings per mol.

E. W. W.

Stereochemistry of *as*-octahydrophenanthrene. J. W. COOK, C. L. HEWETT, and (MRS.) A. M. ROBINSON (J.C.S., 1939, 168—177).—The liquid and cryst., m.p. 95°, hexahydrophenanthrones (A., 1936, 334) are reduced (Clemmensen) to *cis*- (I), b.p. 88—90°/0.1—0.15 mm., and *trans*- (II), m.p. 23—24°, *as*-octahydrophenanthrene, respectively (physical consts. given). The product from the cyclisation of



β -phenylethyl- Δ^1 -cyclohexene (cf. A., 1933, 1042) (washed with 80% H_2SO_4) or from dehydration (P_2O_5) of 1- β -phenylethylcyclohexanol (van de Kamp *et al.*, A., 1936, 1102), when oxidised (CrO_3-AcOH at room temp.) and oximated, affords in either case the oximes, m.p. 176—177° and 124° (in largest amount), of *trans*- and *cis*-keto-octahydrophenanthrenes, respectively, and that, m.p. 187°, of the spirocyclic ketone derived from hydrindene-1-spirocyclohexane (III), thus proving the presence of (I), (II), and (III) (cf. also Perlman *et al.*, A., 1938, II, 57); fractionation does not give homogeneous material (cf. A., 1936, 1102). Although normally (III) is formed in small amount, in one case condensation of mixed hydrocarbons with $(CH_2 \cdot CO)_2O$ gave [from (III)] β -(5- or 6-)cyclohexane-1-spirohydrindoylpropionic acid (IV), m.p. 162—163°, together with, but more resistant to Clemmensen reduction than, β -6-*as*-octahydrophenanthroylpropionic acid (Me ester semicarbazone, m.p. 175.5—176.5°). In one case, Clemmensen reduction gave a small amount of either a mol. compound, $C_{18}H_{22}O_3 \cdot C_{18}H_{24}O_2$, m.p. 140—141°, of CO-acid and a butyric acid, or an oxide, $C_{35}H_{44}O_5$, formed by dehydration of a pinacol reduction product of (IV). (IV) can be separated without previous reduction, by successive formation of Na salt, free acid, Me ester (CH_2N_2) and its semicarbazone, m.p. 186°, and hydrolysis ($EtOH$ -aq. H_2SO_4 , then -NaOH) to (IV). The semicarbazone, m.p. 207°, of (IV) and $EtOH-NaOEt$ give γ -(5 or 6-)cyclohexane-1-spirohydrindylbutyric acid, m.p. 105—107°, cyclised by H_2SO_4 at 100° to 1'-(or 4')-keto-1':2':3':4'-tetrahydro-5:6-benzhydrindene-1-spirocyclohexane (V) (cf. A.), m.p. 109—110°. Oxidation (dil. HNO_3 at 170—180°) of (V) gives pyromellitic acid. (V) and $MgMeI$ give



a product, dehydrogenated (Pt-black) at 295—300° to 1'-(or 4')-methyl-5:6-benzhydryndene-1-spirocyclohexane, m.p. 109—110°. The liquid hexahydrophenanthrene (*loc. cit.*) and $\text{KNO}_3\text{--H}_2\text{SO}_4$ give cis-7-nitro-9-keto-1:2:3:4:9:10:11:12-octahydrophenanthrene, m.p. 151.5—152°, reduced (H_2 , Pd-black, COMe_2) to the 7- NH_2 -derivative, m.p. 118.5—119° (*Ac* derivative, m.p. 178—179°), converted (diazo-reaction) into the 7-OH-compound (VI), m.p. 141—142° (semicarbazone, m.p. 233—234°), oxidised (KMnO_4) to adipic, glutaric, and oxalic acids, and (in one case, in cold KOH) to (?) *trans*-hexahydrophthalic acid, which may be formed from the *cis*-ester. No *cis*-hexahydrohomophthalic acid (*p*-phenylphenacyl ester, m.p. 146—147°) was isolated; the *p*-bromophenacyl ester of the *trans*-acid has m.p. 178—179°. (VI) is reduced (Clemmensen) to cis-7-hydroxy-1:2:3:4:9:10:11:12-octahydrophenanthrene (VII), m.p. 94—95° (benzoate, m.p. 100—101°; 3:5-dinitrobenzoate, m.p. 165.5—166.5°). Its liquid Me ether is dehydrogenated (Pt-black) at 300° to 7-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 60—61° (picrate, m.p. 125.5—126.5°), dehydrogenated further by Se at 300° to 2-methoxyphenanthrene. 2-Phenyl- Δ^1 -cyclohexenylacetic acid is dehydrated (cold H_2SO_4) to 9-hydroxy-1:2:3:4-tetrahydrophenanthrene (3:5-dinitrobenzoate, m.p. 220°). 2-Phenylcyclohexanolacetic acid and Ac_2O give 2-phenylcyclohexylideneacetic acid, m.p. 168—169°, but hydrogenation does not yield the saturated *trans*-acid in useful amount. Hydrogenation (PtO_2 , AcOH) of (VI) gives (VII), 2:10-dihydroxy-, m.p. 239—240°, and 2-hydroxy-perhydrophenanthrene (VIII), m.p. 108—109° (3:5-dinitrobenzoate, m.p. 167—168°) [also by hydrogenation of (VII)], and perhydrophenanthrenes, b.p. 133—135°/13—14 mm. (probably a mixture of stereoisomerides). The latter and Se at 300—315° readily give phenanthrene (*cf.* Pinkney *et al.*, A., 1936, 1101). (VIII) and $\text{CrO}_3\text{--AcOH}$ at room temp. give a ketone [semicarbazone (IX), m.p. 179—180°] and a dicarboxylic acid, $\text{C}_{14}\text{H}_{22}\text{O}_4$, m.p. 170°. In an oxidation of the crude carbinol, a resultant semicarbazone had m.p. 209—210° [isomeric with (IX)]. cycloHexanone and Mg β -*m*-anisylethyl chloride give β -*m*-anisylethylcyclohexanol, b.p. 160—165°/0.5 mm. (3:5-dinitrobenzoate, m.p. 93.5—94.5°), dehydrated by KHSO_4 at 160° to the Δ^1 -cyclohexene (X), b.p. 185°/22 mm., hydrogenated in EtOH (Pd-black) to the corresponding cyclohexane, b.p. 120—125°/0.5 mm. The latter is demethylated (HBr--AcOH) to a compound, b.p. 145—147°/0.8 mm., hydrogenated (PtO_2 , AcOH) to β -3'-hydroxycyclohexylethylcyclohexane (XI), m.p. 57—58° (3:5-dinitrobenzoate, m.p. 105.5—106.5°). (X) and $\text{AlCl}_3\text{--CS}_2$ at 0° give a product [Se at 300° gives some 2-methoxyphenanthrene], demethylated (HBr--AcOH) to 5-hydroxyhydryndene-1-spirocyclohexane (XII), m.p. 96—97° (benzoate, m.p. 103.5—104.5°; 3:5-dinitrobenzoate, m.p. 146—147°; CH_2N_2 gives the Me ether, b.p. 120°/0.15 mm., resistant to Pt-black at 300°). X-Ray crystallographic data for (VII), (VIII), (XI), and (XII) are recorded. A. T. P.

Photo-oxides of 9:10-dixenylanthracene and 9:10-diphenyl-2-methylanthracene. D. DUVEEN and A. WILLEMART (J.C.S., 1939, 116—118).—*p*-

$\text{LiC}_6\text{H}_4\text{Ph}$ (from *p*- $\text{C}_6\text{H}_4\text{PhBr}$ and Li in Et_2O and N_2) with anthraquinone gives 9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene, m.p. 210—212°, converted by KI--AcOH into 9:10-di-*p*-xenylanthracene (I), m.p. ~415° (all m.p. on Cu block). Insolation of (I) in CS_2 gives a photo-oxide, $\text{C}_{38}\text{H}_{26}\text{O}_2$, which liberates O_2 (95%) at 190—200° in a vac.; the residue is (I). 2-Methylantraquinone and MgPhBr give 9:10-dihydroxy-9:10-diphenyl-2-methyl-9:10-dihydroanthracene, new m.p. 246°, reduced by KI--AcOH to 9:10-diphenyl-2-methylantraquinone (II), m.p. 242—243°, which affords (as above) a photo-oxide, $\text{C}_{27}\text{H}_{20}\text{O}_2$, which liberates O_2 (94%) at 170—175° in a vac. The absorption spectra of (I) and (II) are determined. (I) gives colourless solutions in org. solvents and no indication of a diradical form is noted (*cf.* Dufraisse *et al.*, A., 1939, II, 55). A. T. P.

8-Methyl-1:2-benzanthracene. L. F. FIESER and W. S. JOHNSON (J. Amer. Chem. Soc., 1939, 61, 168—171).—9:10-Dihydrophenanthrene is best prepared by $\text{H}_2\text{--Cu}$ chromite without a solvent at 160°. β -9:10-Dihydro-2-phenanthrolylpropionic acid (modified prep.), m.p. 157—158°, gives γ -9:10-dihydro-2-phenanthrylbutyric acid, m.p. 92—92.5°, and thence by $\text{ZnCl}_2\text{--Ac}_2\text{O--AcOH}$, H_2SO_4 , or (best) $\text{PCl}_5\text{--C}_6\text{H}_6\text{--AlCl}_3$ 8-keto-3:4:5:6:7:8-hexahydro-1:2-benzanthracene (I), interconvertible forms, m.p. 97—98° and 92° (*cf.* Burger *et al.*, A., 1937, II, 423). With MgMeCl , (I) gives, after dehydration at 130—160°/1 mm., 8-methyl-3:4:5:6-tetrahydro-1:2-benzanthracene, m.p. 70—70.5° (picrate, m.p. 140—141°), and thence by S at 230—240° or Se at 300° 8-methyl-1:2-benzanthracene (II), forms, m.p. 113.5—114° and 118—118.5° [picrate, m.p. 159.5—160°; $\text{C}_6\text{H}_3(\text{NO}_2)_3$ additive compound, m.p. 169.5—170°; quinone, m.p. 196.5—197° (quinol diacetate, m.p. 202.5—203.7°)]. Cook's (II) (A., 1938, II, 227) was thus impure. When treated first with NaOEt and then with S, the semicarbazone of (I) gives 1:2-benzanthracene. M.p. are corr. R. S. C.

Syntheses of meso-substituted 1:2-benzanthracene derivatives. L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1939, 61, 136—142).—Several preps. of 1':9-dimethyl-1:2-benzanthracenes are prevented by steric hindrance. 8:1- $\text{C}_{10}\text{H}_6\text{Br--NH}_2$ [prep. in 42% yield from 1:8- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$ through the azimide] gives (diazo-reaction) 68% of 1-bromo-8-iodonaphthalene, m.p. 99—100°, the Mg derivative from which with Me_2SO_4 in $\text{Et}_2\text{O--C}_6\text{H}_6$ gives 74% of 1:8- $\text{C}_{10}\text{H}_6\text{MeBr}$ (I), m.p. 77—78°. 1:8- $\text{C}_{10}\text{H}_6\text{Br}_2$ (obtained from the Br-amine), new m.p. 109—110°, reacts very slowly with Mg. 1:8- $\text{C}_{10}\text{H}_6\text{Cl--NO}_2$ gives 1:8- $\text{C}_{10}\text{H}_6\text{Cl--NH}_2$ and thence 1:8- $\text{C}_{10}\text{H}_6\text{ClBr}$, new m.p. 96.5—97° (picrate, m.p. 130.5—131.5°), which affords 8-chloro-1-methylnaphthalene, m.p. 68—69°, b.p. 125°/4 mm. (picrate, m.p. 138.5—139.5°). 1:4- $\text{C}_{10}\text{H}_6\text{Me--SO}_3\text{K}$ (prep. described) and Br--NaBr give 1:4- $\text{C}_{10}\text{H}_6\text{MeBr}$ (II), new m.p. 7° (picrate, m.p. 128—129°). 1:7- $\text{C}_{10}\text{H}_6\text{Me--CO--C}_6\text{H}_4\text{--CO}_2\text{H--O}$ could not be converted into the benzanthranyl acetate. *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ and the Mg derivative from (I) give 66% of *o*-8-methyl-1-naphthoylbenzoic acid, m.p. 231.5—232.5°; this or its Me ester, m.p. 153—154° does not add MgMeCl

smoothly at the CO. *o*-C₆H₄Cl-COME (III) (prep. from *o*-C₆H₄Cl-CHO and MgMeCl with subsequent oxidation by Na₂Cr₂O₇-HCl) with the Mg derivative of (II) gives a carbinol, converted by KHSO₄ at 200° into 4-*α*-*o*-chlorophenylvinyl-1-methylnaphthalene, b.p. ~200°/4 mm., hydrogenated (PtO₂) in AcOH to 1-*α*-*o*-chlorophenylethyl-4-methylnaphthalene, m.p. 66.5—67.5°, which with CuCN in aq. C₅H₅N at 220° gives 1-*α*-*o*-carbamyphenylethyl-4-methylnaphthalene, m.p. 171—172°. Hydrolysis thereof by iso-C₅H₁₁O-NO-AcOH at 40° gives the *o*-carboxylic acid, m.p. 190.5—191.5°, which with ZnCl₂-Ac₂O-AcOH gives an acetate, reduced by Zn-aq. NaOH-PhMe to 3:9-dimethyl-1:2-benzanthracene, m.p. 93—93.5° [picrate, m.p. 137—138°; C₆H₅(NO₂)₃ additive compound, m.p. 145°; oxidised to 3-methyl-1:2-benzanthraquinone, new m.p. 178.5—179.5°]. However, a similar synthesis with (III) and (I) gives only 20% of vinyl compound; the reduced product could not be converted into a nitrile. The Mg derivative of (I) with *o*-C₆H₄Cl-CHO in C₆H₆ gives 44% of *o*-chlorophenyl-8-methyl-1-naphthylcarbinol, b.p. 210°/4 mm., oxidised to *o*-C₆H₄Cl-8:1-C₁₀H₆Me ketone, b.p. 205°/4 mm., which is also obtained from the same Mg derivative and *o*-C₆H₄Cl-CN by way of the ketimine and gives impure materials with MgMeCl, followed by KHSO₄ and H₂. M.p. are corr.

R. S. C.

Synthesis of compounds related to 1:2-benzanthracene and cholanthrene. W. E. BACHMANN (J. Org. Chem., 1938, 3, 434—447).—5-Keto-5:6:7:8-tetrahydro-1:2-benzanthracene (I) (modified prep. from *γ*-3-phenanthrylbutyric acid described) is reduced [Al(OPr)₃ in Pr²OH] to 5-hydroxy-5:6:7:8-tetrahydro-1:2-benzanthracene (II), m.p. 125.5—126.5° (acetate, m.p. 136—136.5°; Me ether, colourless plates, m.p. 76—77°, or colourless needles, m.p. 86.5—87.5°), dehydrated and dehydrogenated by Pd-C at 310° to 1:2-benzanthracene and converted by dry HCl in C₆H₆ containing CaCl₂ into 5-chloro-5:6:7:8-tetrahydro-1:2-benzanthracene (III), m.p. 116°, which passes in boiling C₅H₅N into 7:8-dihydro-1:2-benzanthracene, m.p. 112—113.5° (picrate, m.p. 138—139°), also obtained when (III) is heated at its m.p. or (II) is kept at 200°/15 min. (III) is condensed with CHNa(CO₂Et)₂ and the product is hydrolysed to 5:6:7:8-tetrahydro-1:2-benzanthryl-5-malonic acid, m.p. 175—177° (decomp.), decarboxylated to the -5-acetic acid, m.p. 153—154° (Me ester, m.p. 82—83°), which is transformed by SOCl₂ in Et₂O containing a little C₅H₅N into the corresponding chloride, cyclised (SnCl₄ in CS₂) to 1-keto-2a:3:4:5-tetrahydrocholanthrene (IV), m.p. 193—194° (semipicrate, 2C₂₀H₁₆O, C₆H₅O₇N₃, m.p. 178—178.5°), which is dehydrogenated (S at 220°) to 1-ketocholanthrene. Reduction (Clemmensen) of (IV) gives 2a:3:4:5-tetrahydrocholanthrene, prisms or plates, m.p. 107°, or plates, m.p. 101—101.5°, either of which gives the picrate, m.p. 168—168.5°; it is dehydrogenated to cholanthrene (V). Addition of (I) to Zn and CH₂Br-CO₂Me in Et₂O-C₆H₆ containing a little I and treatment of the product with dil. HCl followed by HCO₂H gives Me 7:8-dihydro-1:2-benzanthryl-5-acetate (VI), m.p. 101.5—102°; the acid, m.p. 193—194° when brought into a bath at 185°, is dehydrogen-

F** (A., II.)

ated by S at 210° to 5-methyl-1:2-benzanthracene and 1:2-benzanthryl-5-acetic acid (VII), m.p. 233—232° (yield 10%). Alternatively (VI) is dehydrogenated by S at 200—205° to Me 1:2-benzanthryl-5-acetate, m.p. 116° (yield 90%), which is hydrolysed to (VII). Oxidation of (VII) by Na₂Cr₂O₇ and boiling AcOH affords 1:2-benzanthraquinonyl-5-acetic acid (Me ester, m.p. 168—169°). Successive treatments of (VII) with PCl₅-C₆H₆ and AlCl₃-CS₂ yield 1-ketocholanthrene, m.p. 230°. Modified directions are given for the conversion of *o*-C₆H₄Cl-CHO into *o*-C₆H₄Cl-CH₂-CH₂-CO₂H and thence into 4-chlorohydrindone, 4-chloro- and 4-cyano-hydrindene. The last with 1-C₁₀H₇-MgBr affords 4-1'-naphthoyl-hydrindene, b.p. 215—220°/0.2 mm., which passes at 410° into (V). meso-Dihydrocholanthrene, m.p. 161.5—162.5°, is obtained by treating (V) with Li or Na in Et₂O-C₆H₆ followed by MeOH. Maleic anhydride and (V) in boiling C₆H₆ slowly yield cholanthrene-6:12b-endo-*αβ*-succinic anhydride, m.p. 232° (decomp.) if brought into bath at 210°, which dissociates in hot xylene, thereby affording pure (V), m.p. 174.5—175° (corr.), in 80% yield.

H. W.

Carcinogenic hydrocarbons. III. 20-isopropylcholanthrene. Fluorescence and crystal forms of methyl-, ethyl-, and isopropyl-cholanthrene. W. F. BRUCE and F. TODD (J. Amer. Chem. Soc., 1939, 61, 157—161; cf. A., 1938, II, 271).—Pr²Cl, PhBr, and AlCl₃ at 0° give *p*-bromocumene (I) (67%), b.p. 87—89°/9 mm., 215—216°/744 mm., and 20% of 4-bromo-1:3-diisopropylbenzene, b.p. 115—118°/9 mm., oxidised to 4:1:3-C₆H₃Br(CO₂H)₂. With (CH₂O)₃ and ZnCl₂, (I) gives 76% of mixed bromoisopropylbenzyl chlorides, b.p. 136—139°/9 mm. (and 8% of a bromoisopropylbenzylidene dichloride, m.p. 86—87.5°), and thence Et₂ bromoisopropylbenzylmalonate, b.p. 163—168°/1 mm., the corresponding acids, m.p. 124—126° [Na H salt, m.p. 236—237° (decomp.)], *β*-bromoisopropylpropionic acids, m.p. 56—58°, b.p. 216—218°/22 mm., bromoisopropylhydrindones, m.p. 90—94°, b.p. 168—170°/9 mm.; and 4-bromo-7-isopropylhydrindene (II), b.p. 120—123°/3 mm. With CuCN in C₅H₅N at 180° (II) gives 4-cyano-7-isopropylhydrindene, b.p. 113—115°/0.8 mm., converted by 1-C₁₀H₇-MgBr in Et₂O into the ketimine hydrochloride, m.p. 262° (decomp.), of 4-*α*-naphthoyl-7-isopropylhydrindene (III), b.p. 210—212°/0.8 mm.; (III) is pyrolysed at 410—415° to 20-isopropylcholanthrene (IV), m.p. 188—189° (corr.). The Mg derivative of (II) and *α*-C₁₀H₇-COCl in Et₂O at -5° give a poor yield of (III) with some 4-isopropylhydrindene, b.p. 88—90°/1 mm., and (*α*-C₁₀H₇-CO)₂O (cf. A., 1938, II, 443). The crystalloptical properties and fluorescence of (IV), 20-methyl- (dimorphic) and 20-ethyl-cholanthrene are described.

R. S. C.

Preparation of $\Delta^{3:5}$ - and $\Delta^{4:6}$ -cholestadienes. Cholesterylene and "7-dehydrocholestene isomeride." J. C. ECK, R. L. VAN PEURSEM, and E. W. HOLLINGSWORTH (J. Amer. Chem. Soc., 1939, 61, 171—174).— $\Delta^{3:5}$ -Cholestadiene (1) (prep. from *ψ*-cholestene dibromide and quinoline), m.p. 79.5—80°, [α]_D²⁵ -103.24° in CCl₄, is identical with cholesterylene, [α]_D²⁵ -100.33° to -123.23° according to

the method of prep. (dehydration of cholesterol, *allo*-cholesterol, or their epimerides, removal of HHal from cholesteryl halides, or pyrolytic decomp. of cholesteryl esters). Δ^4 -⁶-Cholestadiene (II) (prep. from α - or β -cholestene dibromide and quinoline), m.p. 84–85°, $[\alpha]_D^{25} +45.77^\circ$ in CCl_4 , is not identical with the hydrocarbon (III), m.p. 91°, $[\alpha]_D^{25} +4.27^\circ$ in CCl_4 , of Dimroth *et al.* (A., 1936, 977). All the hydrocarbons absorb 2 Br and 2 O (from BzO_2H). H_2 -PdO₂ reduces (II) or (III) to a mixture of cholestane and coprostan; Na-CMe₃Et-OH has no effect. $(\text{CH}_3\text{CO})_2\text{O}$ does not add to (II). HCl-EtOH does not isomerise (I) or (II). Possible positions for the ethylenic linkages are discussed. R. S. C.

Derivatives of 3:4-benzpyrene. A. WINDAUS and K. RAICHEL (Annalen, 1939, 537, 157–170).—The acetyl-3:4-benzpyrene (I) (modified prep.) of Windaus and Rennhak (A., 1937, II, 491) is shown to be the 10- or, less probably, the 9-Ac derivative. 3:4-Benzpyrene, Ac₂O, and ZnCl₂ in C₆H₆ at room temp. give (I) and a diacetyl-3:4-benzpyrene, m.p. 244°. With Zn-Hg-HCl-AcOH (I) gives 10-ethyl-3:4-benzpyrene, m.p. 112° (picrate, m.p. 163°), and a (?) pinacolin, C₄₄H₂₈O, m.p. >350°. With MgMeI in C₆H₆-Et₂O (I) gives an oil, converted by vac. distillation with Zn dust into 10-isopropenyl-3:4-benzpyrene, m.p. 114–115° (picrate, m.p. 164–165°). 3:4-Benzpyrene-10-carboxylic acid (II), m.p. ~318–319° {Me ester, m.p. 181° [*loc. cit.*, 151°; 5:8-quinone, m.p. 302° (decomp.)]}, is prepared from (I) by NaOCl in aq. C₅H₅N and converted by way of the hydrazide, m.p. 264–265° (CMe₂ derivative, m.p. 310°), and azido into 10-acetamido- (III), m.p. 309° [5:8-quinone, m.p. 290° (decomp.)], and 10-di-acetamido-3:4-benzpyrene, m.p. 190°. The oxime, m.p. 254°, of (I) with HCl-AcOH-Ac₂O at 100° gives (III) and thence (HCl-EtOH at 140°) 10-amino-3:4-benzpyrene, m.p. 211° [picrate, m.p. 161° (decomp.)]. With CrO₃ in aq. AcOH at 80° (I) gives 10-acetyl-3:4-benzpyrene-5:8-quinone, m.p. ~260° (decomp.), absence of an isomeric (5:10-)quinone indicating blocking of C₁₀ by Ac. (II) is similarly oxidised to a quinone-acid, which at 240°/high vac. gives CO₂ and 3:4-benzpyrene-5:8-quinone, loss of the Ac proving the presence of the Ac at C₉ or C₁₀. With CrO₃ in boiling AcOH (I) gives benzanthr-7-one-3:4-dicarboxylic anhydride. 3:4-Benzpyrene and SO₂Cl₂ in CCl₄ at 75° give the 5-Cl-derivative, m.p. 210°, which with CuCN at 250–340° yields 5-cyano-3:4-benzpyrene, m.p. 236–237°, also obtained by boiling Ac₂O from 3:4-benzpyrene-5-alloxime, m.p. 241–243° (decomp.). R. S. C.

Antispasmodics. I. F. F. BLICKE and E. MONROE. II. F. F. BLICKE and F. B. ZIENTY (J. Amer. Chem. Soc., 1939, 61, 91–93, 93–95).—With the exceptions noted, the following are prepared from an amine and a bromide in EtOH with or without Na₂CO₃. Temp. in parentheses are m.p. of the hydrochlorides. Salts marked * are potent antispasmodics, those marked † are inactive, the remainder being weak antispasmodics.

1. β -cycloHexylethyl-methyl-, b.p. 89–90°/14 mm. (169–170°), -ethyl-, b.p. 100–105°/21 mm. (231–232°), -butyl-, b.p. 120–123°/17 mm. (262–263°),

-allyl-, b.p. 114–116°/18 mm. (235–236°), and -dimethyl-, b.p. 93–94°/28 mm. (238–239°), -amine. cycloHexyl-, b.p. 174–177°/35 mm. (197–198° *), and benzyl- β -cyclohexylethylamine, b.p. 187–189°/20 mm. (227–228°). β -Phenylethyl-ethyl-, b.p. 107–110°/20 mm. (181–182° †), and -allyl-amine, b.p. 123–126°/19 mm. (176–177° †). NN'-Di-(β -phenylethyl)ethylenediamine, b.p. 235–240°/19 mm. (di-hydrochloride, m.p. 306–307°). β -1-Naphthylethyl-methylamine, b.p. 175–177°/20 mm. (164–165°). γ -cycloHexylpropylmethylamine, b.p. 105–108°/20 mm. (167–168°). δ -cycloHexylbutyl-methyl-, b.p. 110–112°/20 mm. (143–144°), -ethyl-, b.p. 131–134°/19 mm. (202–203°), -butyl-, b.p. 150–156°/20 mm. (232–233° *), and -dimethyl-amine, b.p. 131–132°/38 mm. (196–197°). β -cycloPentylethyl-methyl- (159–160°), -dimethyl-, b.p. 79–81°/32 mm. (219–220°), and -diethyl-amine, b.p. 108–110°/37 mm. (121–122°). γ -Phenoxypropylmethylamine, b.p. 137–140°/19 mm. (156–157°). Di- β -cyclohexylethyl-methyl- (prep. without a solvent), b.p. 188–190°/23 mm. (hydrochloride, * m.p. 257–258°; nitrate, m.p. 158–159°; aurichloride, m.p. 166–167°), and -ethyl-amine, b.p. 195–197°/21 mm. (132–133° *). Di- γ -cyclohexylpropyl-, b.p. 200–204°/20 mm. (214–215°), di- δ -cyclohexylbutyl-, b.p. 225–227°/36 mm. (189–190°), di- β -phenylethyl-, b.p. 192–193°/13 mm. (158–159° *), di- β -cyclopentylethyl- (240–241°), and di- γ -phenoxypropyl-, b.p. 245–250°/21 mm. (125–126° *), -methylamine. Di- δ -cyclohexylbutylethylamine, b.p. 230–236°/19 mm. (134–135°). N- β -cycloHexylethylpiperidine, b.p. 139–140°/18 mm. (255–256° †). CPhMe, (CH₂O)₃, and NH₂Me.HCl give NMe(CH₂-CH₂Bz)₂ [hydrochloride, m.p. 191–192° (lit. 162°)].

II. cycloHexylmethyl-methyl-, b.p. 65–66°/13 mm. (193–194°, stimulant), and -ethyl-amine, b.p. 72–73°/12 mm. (249–250°, stimulant). β -cycloHexylethyl- β' -hydroxyethyl-, b.p. 138–142°/7 mm. (163–164° †), -n-, b.p. 106–107°/13 mm. (266–267°, stimulant), and -iso-propyl-, b.p. 102–104°/16 mm. (199–200°), -amyl-, b.p. 109–115°/7 mm. (265–266°), -heptyl-, b.p. 135–140°/7 mm. (242–243° *), - α' -cyclohexylethyl-, b.p. 165–166°/10 mm. (222–223° *), -di-(β -hydroxyethyl)-, b.p. 177–179°/7 mm. (hydrochloride †, an oil; Bz₂ derivative hydrochloride, m.p. 137–138°), and -dibutyl-, b.p. 124–127°/5 mm. (aurichloride, m.p. 127–128°), -amine. Phenyl- β -cyclohexyl-, b.p. 170–173°/9 mm. (122–123°), and di- β -cyclohexylethyl-, b.p. 168–173°/8 mm. (245–246° *), -amine. Dicyclohexylmethyl-methyl-, b.p. 124–125°/4 mm. (240–241°), and -ethyl-amine, b.p. 149–153°/12 mm. (137–138°, stimulant). Di-(β -cyclohexylethyl)- β' -hydroxyethyl-, b.p. 190–193°/5 mm. (112–113° †), -n-, b.p. 160–165°/7 mm. (an oil *), and -iso-propyl-, b.p. 171–174°/7 mm. (an oil *), -butyl-, b.p. 176–178°/7 mm. (an oil), -amyl-, b.p. 178–181°/7 mm. (an oil), -heptyl-, b.p. 197–202°/6 mm. (an oil †), -allyl-, b.p. 170–172°/5 mm. (137–138°, stimulant), and -cyclohexyl-, b.p. 190–193°/5 mm. (166–167°, stimulant), -amine. Phenyl-, b.p. 213–218°/5 mm. (149–150°), and benzyl-di-(β -cyclohexylethyl)amine, b.p. 207–210°/5 mm. (142–143°, stimulant). Tri-(β -cyclohexylethyl)amine, b.p. 200–208°/6 mm. (233–234°). Dicyclohexyl- β -cyclohexyl-

ethyl-, b.p. 180—182°/5 mm. (172—173°*), and *α*-methylamine, b.p. 178—181°/20 mm. (113—114°). *cyclo*-Hexyl Me ketone and HCO_2NH_2 , when heated gradually to 180°, give *α*-cyclohexylethylamine, b.p. 66—67°/14 mm. (237—238°), and *di*-(*α*-cyclohexylethyl)amine, b.p. 140—142°/4 mm. (304—305°). *Di*-cyclohexyl-, b.p. 131—133°/13 mm. (193—194°), and *di*-(*α*-cyclohexylethyl)-methylamine, b.p. 167—169°/12 mm. (179—180°), are obtained from the *sec.* bases by CH_2O .

R. S. C.

Syntheses of spasmolytically active substances. W. BUTH, F. KÜLZ, and K. W. ROSENMUND (Ber., 1939, 72, [B], 19—28).—A series of *di*- β -phenylethylamines (I) has been investigated in the hope that the physiological properties of papaverine (II) would not be greatly modified by the opening of the heteroring. This is found to be the case. The presence of OMe attached to the ring of (I) is unnecessary but the spasmolytic action, which with many of these compounds exceeds that of (II), is greatly modified by the presence of an α -substituent in the side-chain, the effect increasing in the sequence, Me, Et, Pr, Bu, Ph, CH_2Ph . Physiologically, the solubilities of the compounds now described are not satisfactory. The following *sec.* amines are obtained by suitably heating the requisite primary amine containing Pd-BaSO₄ in H₂ until nearly the theoretical amount of NH₃ has been evolved. *Hydrochlorides* of the following are described: *di*- β -phenylethylamine, m.p. 268—269°; *di*- β -anisylethylamine, m.p. 265—266°; *di*- β -3:4-dimethoxyphenylethylamine, m.p. 199°; *di*- β -3:4-methylenedioxyphenylethylamine, m.p. 262° (free base, m.p. 76°). *Hydrochlorides* of the following bases, obtained by reduction of the requisite amine and CO-compound preferably in MeOH, have been prepared: benzyl- β -phenylethylamine, m.p. 265—266°; β -phenylethyl- β' -*p*-anisylethylamine, m.p. 242—243°; β -phenylethyl- β' -3:4-dimethoxyphenylethylamine, m.p. 189°; β -phenylethyl- β' -3:4-methylenedioxyphenylethylamine, m.p. 242°; β -phenylethyl- β' -phenylisopropylamine, m.p. 160°; β -methoxy- β -phenylethyl- β' -phenylisopropylamine (*r*- and *meso*-forms), m.p. 205° or 150—155°; β -phenylethyl- β' -anisylisopropylamine, m.p. 173° (free base, b.p. 228—229°/17 mm.); β -phenylethyl- β' -3:4-dimethoxyphenylisopropylamine, m.p. 182°; β -phenylethyl- β' -3:4-methylenedioxyphenylisopropylamine, m.p. 200°; β -phenylethyl- β' -methoxy- β' -phenylethylamine, m.p. 146—147° (free base, b.p. 213—215°/15 mm.); *di*-3:4-dimethoxyphenylisopropylamine, m.p. 206—207° (free base, b.p. 254—256°/0.1 mm.). In the prep. of the *hydrochlorides* of the following bases the requisite Schiff's base is hydrogenated under pressure: β -phenylethyl- α' -ethyl- β' -phenylethylamine, m.p. 127° (free base, b.p. 187—189°/12 mm.); β -phenylethyl- α' -propyl- β' -phenylethylamine, m.p. 154°; *di*- β -phenylisopropylamine, *meso*-form, m.p. 254°, and *r*-form, m.p. 197° (the *r*-base, b.p. 185—186°/13 mm., is resolved by *d*- and *l*-camphorsulphonic acid into the \pm -form, $[\alpha]_D^{20} +8^\circ$ in EtOH, and \pm -variety, $[\alpha]_D^{20} -9^\circ$ in EtOH). Reduction of the requisite Schiff's bases by Na and EtOH leads to the *hydrochlorides* of the following amines: β -phenylethyl- α' -isobutyl- β' -phenylethylamine, m.p. 261°; β -phenyl-

ethyl- α' - β' -diphenylethylamine, m.p. 267—268°; β -methoxy- β -phenylethyl- α' - β' -diphenylethylamine, m.p. 256°; β -phenyl- α -benzylethylphenylisopropylamine, m.p. 194°. From the halide and primary amine is obtained *di*- β -methoxy- β -phenylethylamine *hydrochloride*, two forms, m.p. 201° and 234°. H. W.

Preparation of aromatic thiocarbimides.—See B., 1939, 127.

Nitrogenous products formed by chlorination of isothiocarbamides. T. B. JOHNSON and J. M. SPRAGUE (J. Amer. Chem. Soc., 1939, 61, 176—179).—Cyanamide dihydrochloride, $\text{NH}_2\cdot\text{CCl}\cdot\text{NH}_2\cdot\text{HCl}$, m.p. 182—183°, is obtained with $\text{Bu}^+\text{SO}_2\text{Cl}$ or $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Cl}$ (I) by chlorinating $\text{SBu}^+\text{C}(\text{NH}_2)_2\cdot\text{NH}_2\cdot\text{HCl}$ or $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}_2\cdot\text{HCl}$, respectively, and with MeOH at room temp. gives $\text{OMe}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}_2\cdot\text{HCl}$. $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NHMe})_2\cdot\text{NH}_2\cdot\text{HCl}$, an oil (corresponding *picrate*, m.p. 182—183°), with Cl_2 in H_2O at $<20^\circ$ gives (I) and $\text{NHMe}\cdot\text{CN}$. $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NHPh})_2\cdot\text{NH}_2\cdot\text{HCl}$ gives similarly (I) and 2:4-dichlorophenylcyanamide, m.p. 162—163°, also obtained from $\text{NHPH}\cdot\text{CN}$ and Cl_2 in aq. AcOH or 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$, BrCN, and KHCO_3 in abs. EtOH. $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NHPh})_2\cdot\text{NPh}\cdot\text{HCl}$ and Cl_2 in aq. AcOH at $<15^\circ$ give (I) and $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot 2:4)_2$ [also obtained from $\text{SET}\cdot\text{C}(\text{NHPh})_2\cdot\text{NPh}\cdot\text{HCl}$].

R. S. C.

Chemotherapy of bacterial infections. I. Synthesis of derivatives of sulphanilamide. K. GANAPATI (J. Indian Chem. Soc., 1938, 15, 525—531; cf. Kolloff, A., 1938, II, 228).—Synthesis is effected of compounds of general formula, $p\text{-CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHR}$, with a view of testing their Au salts in cases of tuberculosis. $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NCS}$ (I) (1 mol.) and *m*- or *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ (1 mol.) do not afford a monoallylthiocarbamide, but give *m*-, m.p. 95—102° (cf. Lellmann, A., 1884, 49), or *p*-*di*(allylthiocarbamido)benzene, m.p. 200°, respectively. $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ and (I) in EtOH at 100° (bath) afford *N*-*m*-, m.p. 182°, or *p*-acetamidophenyl-*N'*-allylthiocarbamide, m.p. 175°, hydrolysed by aq. HCl (1:1) to the (unstable) *m*- and *p*- NH_2 -derivative, m.p. 118—120° (*dihydrochloride*, m.p. 230°), respectively. (I) and *m*- (with NaOH) or *p*-aminocinnamic acid in EtOH at 100° (bath) give *m*-, m.p. 177° (decomp.), or *p*-allylthiocarbamidocinnamic acid, m.p. 171°, respectively. (I) and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ or *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2\cdot p$ (Gray *et al.*, A., 1937, II, 302) yield similarly *p*-allylthiocarbamidobenzene-sulphonamide, m.p. 182°, and -sulphonanilide-4'-sulphonamide, m.p. 180—181° (decomp.), respectively. $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ (II) and NHMe_2 in C_6H_6 at room temp. afford the *Ac* derivative, m.p. 143°, of *p*-aminobenzenesulphondimethylamide, m.p. 172°; the latter and (I) in EtOH afford *p*-allylthiocarbamidobenzenesulphondimethylamide, m.p. 181°. (II) (1 mol.) and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (2 mols.) in Et_2O give *p*-acetamidobenzenesulphon-*p'*-dimethylaminoanilide, m.p. 196°, hydrolysed to the *p*- NH_2 -derivative, m.p. 231° (cf. Fourneau *et al.*, A., 1938, III, 324), which when heated with (I) affords the corresponding allylthiocarbamido-derivative, m.p. 161°. (II) and $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in H_2O afford the *Ac* derivative,

m.p. $\sim 320^\circ$ (hydrolysed by 6*N*-HCl) of *p*-aminobenzenesulphon-*p*'-aminoanilide, m.p. 155° , converted by boiling with (I) (2 mols.) into a (?) monoallylthiocarbamido-derivative, m.p. 175° . (II) and *m*- or *p*-aminocinnamic acid in H_2O or alkali give m.p. 231° (decomp.), or *p*-, m.p. 252° (decomp.), -*p*'-acetamidobenzenesulphonamidocinnamic acid, respectively, hydrolysed by 40% aq. NaOH at 100° (bath) for 10 min. to *m*-, m.p. 213° , and *p*-, m.p. 239° (decomp.), -*p*'-aminobenzenesulphonoamidocinnamic acid. (II) and $CO_2Et \cdot CH_2 \cdot NH_2 \cdot HCl$ in 2*N*-NaOH-EtOH give *Et p*-acetamidobenzenesulphonamidoacetate, m.p. 129° , hydrolysed (boiling 5*N*-HCl) to the hydrochloride, m.p. 172° (decomp.), of *p*- $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot CO_2H$.

A. T. P.

Preparation of 2:2'-diamino- and -diacetamido-diphenylamines, and their behaviour on oxidation. (MISS M. L. TOMLINSON (J.C.S., 1939, 158—163).—2:2'-Dinitrodiphenylamine and Zn dust in AcOH give 2:2'-diaminodiphenylamine (I), m.p. 101° ; cold Ac_2O in dil. AcOH then gives the Ac_2 derivative, m.p. 199° , stable to mild oxidising agents, converted by boiling Ac_2O into 1-(2'-acetamidophenyl)-2-methylbenziminazole, m.p. 220° . 1:4:3- $C_6H_3MeI \cdot NO_2$, 4:1:3- $NH_2 \cdot C_6H_3Me \cdot NO_2$, K_2CO_3 , and Cu at 160° for 2 hr. give 2:2'-dinitro-4:4'-dimethyldiphenylamine, m.p. 195° which affords the 2:2' (NH_2)₂-derivative (II), m.p. 104° [Ac_2 derivative, m.p. 215° (stable to $FeCl_3$), whence 1-(2'-acetamido-4'-methylphenyl)-2:5-dimethylbenziminazole, m.p. 217°]. *m*-Nitro-*p*-anisidine (III) and 1:4:3- $C_6H_3MeI \cdot NO_2$ similarly afford 2:2'-dinitro-4-methoxy-4'-methyldiphenylamine, m.p. 188° [2:2'-diamine (IV) (Ac_2 derivative, m.p. $181—182^\circ$), 1-(2'-Acetamido-4'-methoxy- (or -methyl)-phenyl)-5-methyl- (or -methoxy)-2-methylbenziminazole has m.p. 202° . α - $C_6H_4Cl \cdot NO_2$ and (III) give 2:2'-dinitro-4-methoxydiphenylamine, m.p. $139—141^\circ$ [diamine (V), m.p. 115° (Ac_2 derivative, m.p. 172°), 2:2'-Diamino-4:4'-dimethoxydiphenylamine (VI), m.p. 100° [Ac_2 derivative (VII), m.p. 233° , whence 5-methoxy-1-(2'-acetamido-4'-methoxyphenyl)-2-methylbenziminazole, m.p. 236° , hydrolysed (HCl) to the 2'- NH_2 -derivative, m.p. 148°], is described. Oxidation (excess of aq. $FeCl_3$ -HCl) of (I), (II), (IV), (V), and (VI) give phenazine and its 2:7- Me_2 , 2-methoxy-7-methyl, m.p. 135° , 2- OMe -, m.p. 123° , and 2:7-(OMe)₂-derivative, m.p. 163° (highly unstable intermediate), respectively, in almost quantitative yields. (VII) and HCl- $FeCl_3$ or - $NaNO_2$ afford 3-acetamido-*N*-(2'-acetamido-4'-methoxyphenyl)-*p*-benzoquinone-4-imine (VIII), m.p. 210° (decomp.), converted by Zn-AcOH into 2:2'-diacetamido-4-hydroxy-4'-methoxydiphenylamine (IX), m.p. 186° and $186—193^\circ$ (dimorphous), reoxidised (atm. O_2) to (VIII) and methylated to (VII). (IX) refluxed with Ac_2O gives 5-methoxy- (or -acetoxy)-1-[2'-acetamido-4'-acetoxy- (or -methoxy)-phenyl]-2-methylbenziminazole, m.p. 244° , hydrolysed (HCl or KOH) to 5-methoxy- (or -hydroxy)-1-[2'-amino-4'-hydroxy- (or -methoxy)-phenyl]-2-methylbenziminazole, m.p. 278° (decomp.), also from (IX) and conc. HCl (reflux). (VIII) and warm, then boiling, conc. HCl give (?) chloro-5-methoxy- (or -hydroxy)-1-[2'-amino-4'-hydroxy- (or -methoxy)-phenyl]-2-methylbenziminazole, m.p. 270° . (VII), (VIII), or

(IX), and cold HNO_3 (*d* 1.43) give a NO_2 -compound, $C_{17}H_{16}O_6N_4$, m.p. 215° (decomp.). The Ac_2 derivative of (IV) and $FeCl_3$ -AcOH give 3-acetamido-*N*-(2'-acetamido-4'-methylphenyl)-*p*-benzoquinone-4-imine (X), m.p. 200° (decomp.) [NO_2 -compound, m.p. 203° (decomp.)], reduced to 2:2'-diacetamido-4-hydroxy-4'-methyldiphenylamine, m.p. 222° , which with Ac_2O gives 1-[2'-acetamido-4'-acetoxy- (or -methyl)-phenyl]-5-methyl- (or -acetoxy)-2-methylbenziminazole, m.p. 243° ; 1-[2'-amino-4'-hydroxy- (or -methyl)-phenyl]-5-methyl- (or -hydroxy)-2-methylbenziminazole has m.p. 248° . (X) and conc. HCl give (?) chloro-1-[2'-amino-4'-hydroxy- (or -methyl)-phenyl]-5-methyl- (or -hydroxy)-2-methylbenziminazole, m.p. 280° .

A. T. P.

Replacement of the diazo- by the acetoxy-group. II. Preparation of *m*-bromophenyl and *m*-iodophenyl acetates. L. E. SMITH and H. L. HALLER (J. Amer. Chem. Soc., 1939, 61, 143—144; cf. A., 1934, 183).—*m*-Bromo-, m.p. 145° , and *m*-iodo-benzenediazonium borofluoride, m.p. 134° , in hot AcOH give *m*-bromo-, b.p. $95—96^\circ/2$ mm., and *m*-iodo-phenyl acetate, b.p. $132—133^\circ/7$ mm., respectively, hydrolysed to the phenols by aq. KOH.

R. S. C.

Condensation of *tert*. aliphatic alcohols with aromatic compounds in the presence of aluminium chloride. IV. *tert*. Dimethylamylcarbinols with phenol. R. C. HUSTON and R. L. GUILLE (J. Amer. Chem. Soc., 1939, 61, 69—71; cf. A., 1939, II, 54).—The isomeric $C_5H_{11} \cdot CMe_2 \cdot OH$, PhOH, and $AlCl_3$ in light petroleum at $25—30^\circ$ give, as sole products (2.1—69.5%), *p*-*tert*-alkylphenols, the structure of which is proved by synthesis of the *tert*-alkylbenzenes from $C_5H_{11} \cdot CMe_2 \cdot OH$, C_5H_6 , and $AlCl_3$, followed by nitration, reduction, diazotisation, and hydrolysis. Oxidation of the NO_2 -derivatives gives *p*- $NO_2 \cdot C_6H_4 \cdot CO_2H$ in all cases. The following appear new: β -*p*-Hydroxyphenyl- β -methyl-*n*-heptane, b.p. $114—117^\circ/2$ mm. (benzoate, m.p. $27—33^\circ$; α -naphthylurethane, m.p. $120—121^\circ$), β -*γ*-, b.p. $111—114^\circ/2$ mm. (benzoate, m.p. $54.2—55.2^\circ$; α -naphthylurethane, m.p. $105—105.5^\circ$), β - δ -, b.p. $113—116^\circ/2$ mm. (benzoate, m.p. $37—38^\circ$; α -naphthylurethane, m.p. $119.5—120.5^\circ$), and β -*ε*-dimethyl-*n*-hexane, b.p. $105—107^\circ/2$ mm. (benzoate, m.p. $46—47^\circ$; α -naphthylurethane, m.p. $132.5—133.5^\circ$), β -methyl- γ -ethyl-, b.p. $109—111^\circ/2$ mm. (benzoate, m.p. $69—70^\circ$; α -naphthylurethane, m.p. $109.5—110.5^\circ$), β - δ -, b.p. $289/741$ mm., m.p. 83° (cf. A., 1934, 999) (benzoate, m.p. $73—74^\circ$; α -naphthylurethane, m.p. $102—103^\circ$), β - γ - δ -, m.p. 74° (benzoate, m.p. $47—48^\circ$; α -naphthylurethane, m.p. $114.5—115.5^\circ$), and β - γ -trimethyl-*n*-pentane, m.p. 160° . β -*p*-Nitrophenyl- β -methyl-*n*-heptane, b.p. $148—150^\circ/2$ mm., β -*γ*-, b.p. $133—135^\circ/2$ mm., β - δ -, b.p. $135—137^\circ/2$ mm., and β -*ε*-dimethyl-*n*-hexane, b.p. $129—131^\circ/2$ mm., β -methyl- γ -ethyl-, b.p. $127—130^\circ/4$ mm., and β - δ -trimethyl-*n*-pentane, b.p. $108—110^\circ/4$ mm., and the corresponding NH_2 -compounds, b.p. $108—111^\circ/2$ mm., $115—119^\circ/4$ mm., $99—101^\circ/2$ mm., $99—102^\circ/2$ mm., $103—106^\circ/2$ mm., and $112—115^\circ/5$ mm., respectively. $CHMePr^a \cdot MgBr$ and $AcCl$ in Et_2O give γ - δ -dimethylpentan- β -one, b.p. $135—140^\circ/744$ mm., which with $MgMeI$ affords β - γ -trimethyl-*n*-

metallic salts such as ZnCl_2 , AlCl_3 , FeCl_3 , SnCl_4 , SbCl_5 , and BF_3 (acid bromides and, particularly, iodides are effective without these catalysts); (6) fission by alkalis or, in certain cases, by NH_3 or amines; (7) fission by alkali metal (Na , K , Na-K ; or Na in liquid NH_3); (8) fission by organo-metallic compounds (Grignard's compounds; LiPh).

H. W.

Free radicals and radical stability. I. Influence of the phenoxy group on radical stability and merisation. II. Dimethoxytriphenylmethyls. S. T. BOWDEN (J.C.S., 1939, 26—33; 33—41).—I. Wieland's observation (A., 1911, i, 851) that definite colour changes occur when $(\text{C}_6\text{H}_5)_2\text{OPh}$ (I), m.p. (vac.) $214.5\text{--}216^\circ$, is heated in a high-boiling solvent (e.g., C_{10}H_8 , EtOBz) in absence of O_2 is confirmed; the intensity increases with rise in temp. but there is no exact reversibility in the colour changes owing to the formation of decomp. products. The thermal behaviour of (I) is analogous to that of diphenylbis(diphenylene)-ethane (II). Dissociation of (I) at 160° gives the radical, $\cdot\text{C}_6\text{H}_5\text{OPh}$, but in much lower concn. than that of $\cdot\text{C}_6\text{H}_5$ in the $(\text{C}_6\text{H}_5)_2$ system at room temp.; the stabilising influence of OPh on the radical is \ll that of Ph . At elevated temp. (I) is converted into $\text{C}_6\text{H}_5(\text{OPh})_2$ and $(\text{C}_6\text{H}_5)_2$. (I) is undissociated in boiling C_6H_6 , does not give coloured solutions in liquid SO_2 , and is photochemically stable. The fundamental characteristic of an ethane derivative to dissociate into radicals is termed "merisation tendency," and two classes of free radical systems are considered, viz., where the tendency is high, e.g., $(\text{C}_6\text{H}_5)_2$ (III), and low, e.g., $(\text{C}_6\text{H}_5)_2\text{OPh}$. At 18° , a solution of (III) in PhBr absorbs 1 mol. of O_2 in 3 min., whereas (I) requires 3 hr. (absorption apparatus described; cf. Gomberg *et al.*, A., 1917, i, 551). The solution of (I) becomes gradually deep yellow, ~ 4 mols. of O_2 are absorbed, and the primary oxidation product is not isolable; (III) forms a colourless peroxide and a yellow oil, each of composition $(\text{C}_6\text{H}_5)_2\text{O}_2$. The rate of dissociation of (II) is 20 times that of (I). A further indication of the varied rates of oxidation of (I) and (II) is afforded by the Prussian-blue test (Conant and Evans, A., 1929, 934). (I) in C_6H_6 does not absorb I at room temp. during 24 hr., but in xylene and CO_2 at 110° absorbs an amount corresponding with 0.28 mol.; $\text{C}_6\text{H}_5(\text{OPh})_2$ does not absorb I. (I) with Na in Et_2O (inert atm.) at room temp. becomes yellow, then deep red (few days), due to formation of Na derivative, but the isomeric $(\text{C}_6\text{H}_5)_2\text{O}$ does not react appreciably under these conditions.

II (cf. Gomberg *et al.*, A., 1925, i, 1266; 1926, 738). 2:4'-Dimethoxytriphenylcarbinol, m.p. 115° (basicity val. 9.9; $\text{C}_6\text{H}_5\text{OH} = 1$), and AcCl or AcBr in light petroleum afford the *chloride* (IV), m.p. 116° , or *bromide*, m.p. 118° , respectively. (IV) and excess of Hg in $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$, then air treatment, afford a *peroxide*, m.p. 139° . Pure (IV) in C_6H_6 and excess of mol. Ag (in CO_2), shaken for 4—6 hr. in the dark, afford a solution of the radical (O_2 absorption determined); evaporation at $40\text{--}45^\circ/70$ mm. (CO_2) gives a pale yellow solid (V), m.p. 80° (vac.) (isomerises with traces of acid) (apparatus for isolation described in detail). It is much more stable than the 2:4-(OMe) $_2$ -analogue

(see below). In non-polar solvents the neutral radical is orange, but the ion in liquid SO_2 is bright red. 2:2'-Dimethoxytriphenylmethyl chloride, m.p. 95° , and *peroxide*, m.p. 110° , are described. The corresponding free radical (VI), m.p. 88° (vac.), forms yellowish-red solutions with non-polar solvents, but the colour in liquid SO_2 is deep brownish-black. Neither (V) nor (VI) gives additive compounds with Et_2O . The mechanism of formation of such derivatives, e.g., from CPh_3 , is discussed; the free radical is probably not responsible. Radical stability is not \propto the no. and orientation of substituted OMe (cf. Burton and Ingold, A., 1929, 1052). Radical stabilities of (V) and (VI) are 28 and 41%, respectively, in C_6H_6 , and 32 and 55% in PhNO_2 (cryoscopic mol. wt. determinations; apparatus described). The thermal stabilities of the corresponding CR_3I are much $<$ that of CPh_3I (apparatus for I absorption described).

A. T. P.

Derivatives of the ethers of hydroxyquinol. H. W. DORN, W. H. WARREN, and J. L. BULLOCK (J. Amer. Chem. Soc., 1939, 61, 144—147).—2:6:1:4-OMe- $\text{C}_6\text{H}_2\text{Br}(\text{OH})_2$ (prep. from vanillin detailed) and Me_2SO_4 give 6-bromo-1:2:4-trimethoxybenzene, m.p. $37\text{--}38^\circ$, converted by $\text{Br}\text{--}\text{C}_6\text{H}_5$ into the 3:6-Br $_2$ -ether (I), m.p. 97° , which is oxidised by HNO_3 (d 1.41) to 3:6-dibromo-2-methoxy-p-benzoquinone, m.p. 172° , converted by $\text{SO}_2\text{--aq. EtOH}$ into 3:6-dibromo-2-methoxyquinol, m.p. 155° (decomp.). With $\text{Br}\text{--AcOH}$ at 100° 5-bromo- gives 3:5:6-tribromo-1:2:4-trimethoxybenzene, m.p. $85\text{--}86^\circ$, stable to $\text{KOH}\text{--EtOH}$. Prep. of $x:1:2:4\text{--NO}_2\text{--C}_6\text{H}_2(\text{OAc})_3$ (II) (Thiele *et al.*, A., 1901, i, 701) gives also some 2:1:4-OH- $\text{C}_6\text{H}_3(\text{OAc})_2$, m.p. 104° . $\text{Me}_2\text{SO}_4\text{--NaOH}$ converts (II) into 5:1:4:2- $\text{NO}_2\text{--C}_6\text{H}_2(\text{OMe})_3$ (III), whence it follows that $x = 5$ and that the dibromonitro-derivative (*loc. cit.*) is 5:3:6:1:2:4- $\text{NO}_2\text{--C}_6\text{H}_2\text{Br}_2(\text{OH})_3$ (IV). The *Me₃ ether*, m.p. 127° , of (IV) with $\text{Sn}\text{--HCl}$ gives 3:6-dibromo-2:4:5-trimethoxyaniline, m.p. 115° , and thence (I). 1:2:4- $\text{C}_6\text{H}_3(\text{OMe})_3$ and warm H_2SO_4 (d 1.8) give 2:4:5-trimethoxybenzenesulphonic acid (chloride, m.p. 130° ; amide, m.p. 76° ; anilide, m.p. 170°), converted by $10\text{N}\text{--HNO}_3$ into (III). Vanillin and 20% oleum give the 5-sulphonic acid, m.p. 124° , converted by $\text{H}_2\text{O}_2\text{--NaOH}$ into 2:5-dihydroxy-3-methoxybenzenesulphonic acid, decomp. 290° , and thence into 2:3:5-trimethoxybenzenesulphonyl chloride, m.p. 98° .

R. S. C.

Derivatives of phloroglucinol trimethyl ether. G. R. RAMAGE, J. L. SIMONSEN, and W. J. I. STOWE (J.C.S., 1939, 89—91; cf. A., 1938, II, 441).—2:4:6:1-(OMe) $_3\text{C}_6\text{H}_2\text{CHO}$ (I) and Zn in AcOH or Ac_2O give 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_3$. (I) is stable to $\text{Al}(\text{OEt})_3$ at room temp. but $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH gives an unstable gum containing (?) 2:4:6:2':4':6'-hexamethoxybenzoin (2:4-dinitrophenylhydrazones, m.p. $275\text{--}276^\circ$). 2:4:6-Trimethoxybenzaldehyde and $\text{H}_2 + \text{Pd}\text{--C}$ in AcOH give 2:4:6:2':4':6'-hexamethoxydibenzylamine (II), m.p. $118\text{--}119^\circ$, but reduction (method: Schales, A., 1935, 1491) affords 2:4:6-trimethoxybenzylamine, (III), m.p. $59\text{--}60^\circ$ [hydrochloride (+7 H_2O), m.p. 92° ; Ac derivative, m.p. $153\text{--}154^\circ$], and a little (II). The nitrite of (III) is decomposed by heat to give mainly

2:4:6:2':4':6'-hexamethoxydiphenylmethane, m.p. 116—117°, also obtained from 1:3:5-C₆H₃(OMe)₃ and 40% CH₂O in EtOH-piperidine acetate at 100° (bath). 3:5:1-(OMe)₂C₆H₃-OH similarly gives an intractable resin. 2:4:6:1-(OMe)₃C₆H₂-CH₂-OH could not be obtained by the method of Freudenberg and Harder (A., 1927, 251). A. T. P.

Nitronaphthyl and aminonaphthyl alkyl sulphides. H. H. HODGSON and E. LEIGH (J.C.S., 1939, 126—128).—The solid mixture of dinitrodinaphthyl mono- and di-sulphides, from C₁₀H₆Cl-NO₂-Na₂S₂-EtOH, is refluxed with Na₂S (cryst.) and aq. NaOH-EtOH (5 min.), the insol. monosulphide filtered off, and the filtrate (A) used as follows. (A) from 1:4- or 2:1-C₁₀H₆Cl-NO₂, in aq. NaOH, i.e., 4:1- or 1:2-NO₂-C₁₀H₆-SNa, respectively, and Me₂SO₄ at 60—65° or 40—45° give 4-nitro-1- (I), m.p. 84.5—85°, and 1-nitro-2- (II), m.p. 120°, -naphthyl Me sulphide, respectively. 2:1-NO₂-C₁₀H₆-SH could be methylated only by heating a paste of the slightly moist Na salt, NaHCO₃, and Me₂SO₄ at 100° (bath) (followed by PbO); 2-nitro-1-naphthyl Me sulphide, has m.p. 104—105°. The corresponding Et sulphide could not be prepared, but 4-nitro-1-, m.p. 63°, and 1-nitro-2-, m.p. 87°, -naphthyl Et sulphides are readily obtained. (I) or (II) and SnCl₂-HCl-AcOH at 100° (bath) give the stannichlorides, decomposed by 5% aq. NaOH at 60° to the respective 4-amino-1-, m.p. 55° [hydrochloride, m.p. ~220° (decomp.)], and 1-amino-2-naphthyl Me sulphide, b.p. 253°/753 mm. [hydrochloride, m.p. ~210° (decomp.)]; stannichloride, decomp. ~195°. Azo-dyes from the former base are deeper (bluer) in shade than those from the latter (cf. A., 1926, 515). Colours of the sulphides with H₂SO₄, ClSO₃H, and oleum are recorded.

A. T. P.

Synthesis of arylsulphonium salts. G. DOUGHERTY and P. D. HAMMOND (J. Amer. Chem. Soc., 1939, 61, 80—81).—Ph₂S and Br-AcOH give (p-C₆H₄Br)₂S and thence by Cl₂-C₆H₆ the dichloride, which with C₆H₆ and AlCl₃ at 80° gives phenyldi-p-bromophenylsulphonium chloride and thence the bromide, iodide, and platinichloride. The derived hydroxide is alkaline and attacks (slightly) Al and Zn. Thianthrene gives similarly phenyl- and p-phenetylthianthronium platinichloride. R. S. C.

Influence of saligenin and its 5-methyl derivative on conductivity of boric acid.—See A., 1939, I, 147.

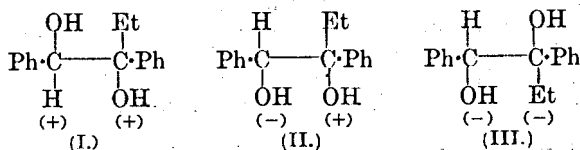
Action of mixed nitric and sulphuric acids on 5-bromo-3:6-dinitro-1:2:4-trimethylbenzene. I. J. RINKES (Rec. trav. chim., 1938, 57, 1405—1409).—The "nitrate," m.p. 150°, obtained by Huender (A., 1915, i, 129) from 1:2:4:5:3:6-C₆Me₃Br(NO₂)₂ is formed by conversion of one of the Me into CH₂-O-NO₂ (cf. Smith *et al.*, A., 1937, II, 338). This benzyl nitrate (I) in EtOH saturated with NH₃ affords the corresponding 5-bromo-3:6-dinitrodimethyl-benzaldehyde, m.p. 190—191° (oxime, m.p. 191—192°), and thence (AgNO₃, aq. EtOH-NaOH at 10°) the -benzoic acid, m.p. 232° (Me ester, m.p. 171°). (I) in EtCO₂H, with boiling H₂SO₄-H₂O (1:1) for 5 min., gives the corresponding -benzyl alcohol, m.p.

202° (cf. Huender, *loc. cit.*), converted by Ac₂O-H₂SO₄ into the acetate, m.p. 102—103°, and by HNO₃ (d 1.5) at 0° into (I). A. T. P.

[Synthesis of condensed polynuclear hydrocarbons by the cyclodehydration of aromatic alcohols. VII. Cyclodehydration involving the Wagner rearrangement.] M. T. BOGERT (J. Org. Chem., 1938, 3, 508).—α-Phenyl-δδ-dimethylpentan-γ-ol and its phenylurethane have been described previously by Hill and Bruce (A., 1930, 343).

H. W.

Stereochemical structure. IX. Stereochemical relationship of the α- and β-forms of substituted hydrobenzoin. (b) Ethylhydrobenzoin (β-form). R. ROGER (J.C.S., 1939, 108—111; cf. A., 1937, II, 415).—(−)-Ethylhydrobenzoin (β-form) (I), m.p. 96—97°, [α]_D²⁰ −31.5° in COMe₂, and MgEtI, then PhCHO-C₆H₅, afford (+)-ethylbenzoin, m.p. 71—72°, [α]_D²⁰ +25.4° in EtOH. Controls with (+)- (β-form, m.p. 96—97°) or partly racemised (−)-ethylhydrobenzoin (α-form, m.p. 88—90°), and MgEtI, show that no change in form occurs under the conditions (vals. of [α] unchanged). The deduction can be made that the β-form of (+)-ethylhydrobenzoin would undergo oxidation to (−)-ethylbenzoin. Configurations (II) and (III) are assigned to the α- and β-forms of (+)-ethylhydrobenzoin, respectively, which



are diastereoisomeric (cf. McKenzie *et al.*, J.C.S., 1910, 97, 473), as also are the α- and β-forms of the (−)-glycol. The method of synthesis of such α- and β-forms is discussed, and also whether formation of optically active ethylbenzoin can be regarded as example of "asymmetric synthesis" (cf. McKenzie, "Ergebnisse der Enzymforschung," V, p. 4, Leipzig, 1936). A. T. P.

Rate of pinacolin isomerisation of two cis-trans-isomeric pinacols. R. CRIEGEE and K. H. PLATE (Ber., 1939, 72, [B], 178—181).—The rate of isomerisation of cis- (I) and trans- (II) -7:8-diphenylacenaphthene-7:8-diol by CCl₃-CO₂H or p-C₆H₄Me-SO₃H in AcOH has been measured by treating aliquot portions of the solution after definite intervals with NaOAc in AcOH followed by excess of Pb(OAc)₄; after completion of the oxidation of unchanged diol the unused Pb(OAc)₄ is determined iodometrically. The isomerisation is apparently unimol., variation in the const. being attributed to experimental error. The half period of the transformation of (I) in presence of 0.1N-p-C₆H₄Me-SO₃H at 20° is 7 min., whereas that of (V) is 23 min. The rate is approx. ∝ the concn. of the catalyst, CCl₃-CO₂H being much less efficient than p-C₆H₄Me-SO₃H. Under sufficiently energetic conditions, the solvent AcOH can cause isomerisation, which is noticeable after some days at room temp. The temp. coeff. is 3.6 in the case of (I). H. W.

Replaceability of aromatically united bromine by lithium by means of lithium phenyl. G. WITTIG and U. PÖCKELS (Ber., 1939, 72, [B], 89—92; cf. A., 1938, II, 441).—4 : 6 : 1 : 3- $C_6H_2Br_2(OMe)_2$ is slowly converted by LiPh in Et_2O at room temp. into the Li_2 compound; hydrolysis of the reaction mixture gives PhBr, 1 : 3- $C_6H_4(OMe)_2$, and a little 4 : 1 : 3- $C_6H_3Br(OMe)_2$ (I). The successive action of LiPh and CO_2 on (I) leads to 2 : 4-(OMe) $_2C_6H_3CO_2H$, 2 : 2' : 4 : 4'-tetramethoxybenzophenone, new m.p. 137.2—139.5°, and tri-2 : 4-dimethoxyphenylcarbinol. Addition of $COPH_2$ to the product from LiPh and (I) gives 2 : 4-dimethoxytriphenylcarbinol, m.p. 137.8—138.6°, whence the 5-Br-derivative, m.p. 192.8—193.8°. $m-C_6H_4(OMe)_2$ is converted by successive treatments with LiPh and CO_2 in Et_2O into 2 : 6-(OMe) $_2C_6H_3CO_2H$ and 2 : 2' : 6 : 6'-tetramethoxybenzophenone, m.p. 205.4—206.2°. 5 : 5'-Dibromo-2 : 2' : 4 : 4'-tetramethoxybenzophenone, m.p. 224.2—225.2°, and tri-(5-bromo-2 : 4-dimethoxyphenyl)-carbinol, m.p. 255.5—256.5°, were prepared.

H. W.

Cisoid and transoid character of epimeric alcohols of the steroid series. K. MIESCHER and W. H. FISCHER (Chem. and Ind., 1939, 113—114; cf. A., 1938, II, 174).—Objections to the nomenclature of Schoenheimer and Evans (A., 1936, 1105) are overcome if $C_{30}OH$ is referred to C_{29} . Opposite conclusions can be drawn regarding the steric character of the OH in coprosterol and epicoprosterol according to the reactions taken as criteria (cf. Ruzicka *et al.*, A., 1938, II, 276). The total influence of substituent groups varies according to the reagent used.

H. B.

Brassicasterol. I. Empirical formula and hydrogenation. E. FERNHOLZ and H. E. STAVELY (J. Amer. Chem. Soc., 1939, 61, 142—143).—Brassicasterol [acetate, m.p. 152°, $[\alpha]_D^{25} -65^\circ$ in $CHCl_3$, obtained by debromination of its tetrabromide, m.p. 205° (decomp.)] is shown to be $C_{29}H_{48}O$ by analysis of its 3 : 5-dinitrobenzoate, m.p. 219°, $[\alpha]_D^{25} -28^\circ$ in $CHCl_3$, and hydrogenation (Pd-black) in EtOH to brassicasteranol (+ α -EtOH), m.p. 142°, $[\alpha]_D^{25} +23.6^\circ$ in $CHCl_3$ (acetate, m.p. 143°, $[\alpha]_D^{25} +14.5^\circ$ in $CHCl_3$; 3 : 5-dinitrobenzoate, m.p. 202°, $[\alpha]_D^{25} +13.9^\circ$ in C_6H_6), which differs from stigmastanol.

R. S. C.

Ultra-violet irradiation of $\Delta^{5,7}$ -androstadiene-3 : 17-diol. K. DIMROTH and J. PALAND (Ber., 1939, 72, [B], 187—190).—Parallel exposure of $\Delta^{5,7}$ -androstadiene-3 : 17-diol (I) and ergosterol (II) to the Hg light causes exactly similar changes in the absorption spectra so that it is certain that analogous irradiation products result from (I) and (II) or other provitamins. Irradiated (I) is devoid of antirachitic action.

H. W.

Isomerism of allopregnane-3 : 20-tetraol. A. SERINI and W. LODGMANN (Naturwiss., 1938, 26, 840; cf. A., 1938, II, 322).—17-Vinylisoandrosterane-3 : 17-diol is converted by Dimroth's method (A., 1938, II, 326) into Δ^{17} -allopregnane-3 : 21-diol, m.p. 203—205° (diacetate, m.p. 156°), which with OsO_4 affords the allopregnane-3 : 17 : 20 : 21-tetraol (= substance K, m.p. 198—200°) of Steiger and Reichstein (*ibid.*, 278).

J. L. D.

Hydroxyalkylammonium mandelates.—See B., 1939, 216.

Perkin reaction. IV. Condensation of carboxylic acids and aldehydes. S. ISHIKAWA and H. TAKEUCHI (Sci. Rep. Tokyo Bunrika Daigaku, 1938, A, 3, 231—237; cf. A., 1935, 1497).— CH_2PhCO_2H (1.3 mols.), PhCHO (1 mol.), and NEt_3 (0.3 mol.) at 180° give 27% of $CHPh:CPhCO_2H$. AcOH and CH_2ClCO_2H do not condense with PhCHO and NEt_3 at 180°, but AcOH, $o-C_6H_4ClCHO$, and NEt_3 give 1% of *trans*- $o-C_6H_4ClCH:CHCO_2H$. CH_2PhCO_2H and $o-C_6H_4ClCHO$ in CO_2 at 200° without a catalyst give 14% of α -phenyl- β -*o*-chlorophenylacrylic acid, m.p. 175.2° (corr.; block). The reaction mechanism is discussed.

R. S. C.

Derivatives of β -naphthaldehyde. J. D. FULTON and R. ROBINSON (J.C.S., 1939, 200—201).— $\beta-C_{10}H_7CHO$ (I), m.p. 58° [prep. from $\beta-C_{10}H_7CN$ (method: Stephen, A., 1925, i, 1131)], and $KCN \cdot H_2O \cdot EtOH$ give β -naphthoin (II), m.p. 125—126° (oxime, m.p. 172°; Me other, m.p. 82°), converted by Fehling's solution into β -naphthol, m.p. 158—159° (whence 2 : 3-di- β -naphthylquinoxaline, m.p. 192—193°). (II) is reduced by 4% Na-Hg in EtOH to hydro-, m.p. 253°, or by Zn-HCl-EtOH to deoxy- β -naphthoin, m.p. 155—156°. (I) and $CH_2(CO_2H)_2 \cdot AcOH$ at 100° (bath) give β -naphthylidenemalononic acid (III), m.p. 207° (decomp.); thermal decomp. then affords β -naphthylacrylic acid, new m.p. 208—209°, also obtained from (I) and $CH_2(CO_2H)_2 \cdot C_5H_5N$ at 100° (bath) for 1½ hr., then boiling (10 min.). (III) and Na-Hg in EtOH give (β -naphthylmethyl)malonic acid, decomp. 150—153°. (I) and $CN \cdot CH_2CO_2Et$, gently heated in presence of a little morpholine, give *Et* α -cyano- β -naphthylidenemalonate, m.p. 125—126° (shrinks at 117°). β -Naphthylidenephenyliisooxazolone heated with 2% aq. Na_2CO_3 affords α -benzamido- β -2-naphthylacrylic acid, new m.p. 240° (previous softening) (cf. Kikkaji, A., 1911, ii, 909) [Me ester, m.p. 142° (previous softening)]; with hot 10% aq. NaOH, 2- $C_{10}H_7Me$ or β -naphthylpyruvic acid, new m.p. 190° (decomp.) [whence 2-hydroxy-3-(β -naphthylmethyl)quinoxaline, m.p. 222—223°], results. The latter acid is oxidised (H_2O_2 , aq. NaOH) to $\beta-C_{10}H_7CH_2CO_2H$, new m.p. 141—142°. A. T. P.

α -(*p*-Aminobenzenesulphonamido)-acids and their derivatives. F. P. MAZZA and C. MIGLIARDI (Atti R. Accad. Lincei, 1938, [vi], 28, 152—157).—The following are prepared, using $p-NHAc \cdot C_6H_4SO_3Cl$: *p*-acetamidobenzenesulphonyl-glycine, m.p. 236°, -alanine, m.p. 208°, and -tyrosine, m.p. 221—222°, hydrolysed respectively to *p*-aminobenzenesulphonyl-glycine (I), m.p. 150°, -alanine (II), m.p. 107—108°, and -tyrosine (III), m.p. 230° (decomp.). With diazotised $p-NH_2 \cdot C_6H_4AsO_3H_2$ (III) gives 3-*p*-arsinobenzenazo-N-*p*-aminobenzenesulphonyl-tyrosine, m.p. <300°. Diazotised (I), (II), and (III) with $m-C_6H_4(NH_2)_2$ give *p*-(2' : 4'-diaminobenzenazo)-benzenesulphonyl-glycine, m.p. 118—119° (decomp.), -alanine, m.p. 114° (decomp.), and -tyrosine, m.p. 158—160° (decomp.). Similarly *p*-(7'-amino-3'-sulpho-1'-naphthol-2'-azo)benzenesulphonyl-glycine, -alanine, and -tyrosine (all m.p. <300°) are obtained.

E. W. W.

Diaroyl peroxides.—See B., 1939, 128.

Kinetics of decomposition of trinitrobenzoates in ethyl alcohol.—See A., 1939, I, 150.

"Oxidising" actions of alkalis. V. Cresols. G. LOCK and F. STITZ (Ber., 1939, 72, [B], 77—82; cf. A., 1930, 597, 775).—In an open Ni crucible, *o*-cresol (I) is converted by KOH-NaOH at about 300—310° fairly rapidly into *o*-OH-C₆H₄-CO₂H (II), the yield of which may attain about 80%. Under similar conditions but in a Ag tube under N₂ (I) is almost completely unchanged whereas in air, H₂ and (II) are produced in the mol. ratio, 3:1. The experiments are not invariably reproducible. At a higher temp. the yield of H₂ increases whereas that of (II) declines in favour of CO₂. The change is apparently: $\text{OK} \cdot \text{C}_6\text{H}_4\text{Me} + 3\text{KOH} = 3\text{H}_2 + \text{OK} \cdot \text{C}_6\text{H}_4\text{C(OK)}_3$. At 300° KOBz is more extensively decomposed than NaOBz whilst at 400° decomp. is complete. NaOBz remains colourless whilst C₆H₅ is produced whereas KOBz is completely carbonised with production of Ph₂. PhMe is scarcely changed by soda-lime at 400° or 550°. MeOH appears to behave like the cresols giving H₂ and Na₂CO₃.

H. W.

Theory of allyl isomerisation. II. O. MUMM, H. HURNHARDT, and J. DIEDERICHSEN (Ber., 1939, 72, [B], 100—111; cf. A., 1938, II, 21).—Evidence is adduced in favour of the view that the wandering of the allyl residue from O to the *para*-C is accompanied in certain cases by a reversal of the unsaturated residue. 2:3:1-OH-C₆H₃Me-CO₂Me is converted by the successive action of NaOMe and α -chloro- Δ^6 -pentene into *Me* 2- Δ^6 -pentyloxy-*m*-toluate (I), b.p. ~125°/1.1 mm., and by that of NaOMe and γ -chloro- Δ^6 -pentene into *Me* 2- α -ethylallyloxy-*m*-toluate (II), b.p. 125—128°/0.8—1.2 mm. (I) is hydrolysed by KOH-MeOH to 2- Δ^6 -pentyloxy-*m*-toluic acid, m.p. 63—64°, whereas (II) gives 2-hydroxy-5-ethylallyl-*m*-toluic acid (III), m.p. 116°. Hydrogenation (colloidal Pd in MeOH) of (I) or (II) affords 2:3:1-OH-C₆H₃Me-CO₂Me. In boiling NPhEt₃, *Me* 2-hydroxy-5-ethylallyl-*m*-toluate (IV), b.p. 170—175°/17 mm. [hydrolysed to (III)], is obtained from (I) or (II). Hydrogenation (colloidal Pd in MeOH) of (III) gives 2-hydroxy-5-amyl-*m*-toluic acid, m.p. 84°. Ozonisation of (IV) in EtOAc at -20° to -12° and hydrogenation (Pd-CaCO₃ in EtOAc) of the ozonide affords a little CH₂O and an aldehyde, oxidised by KMnO₄ to 1-*Me* 3-*H* 6-hydroxy-5-methylisophthalate, m.p. 241°. Decarboxylation of (III) in boiling NPhMe₃ leads to 2-methyl-4-pentenylphenol, converted by 33% NaOH and 50% CH₂Cl-CO₂H into 2-methyl-4-ethylallylphenoxycetic acid, m.p. 112°, oxidised by KMnO₄ in aq. COMe₃ at 0° to 4-carboxy-2-methylphenoxycetic acid, m.p. 285—288°. Attempts to identify the side-chain as a homoallyl or homopropenyl residue are described.

H. W.

Anomalies encountered in the synthesis of tetraphenylfulgenic anhydride. C. F. KOELSCH and H. J. RICHTER (J. Org. Chem., 1938, 3, 473—479).—The condensation of CPh₂ with Et₂ diphenylitaconate in presence of NaOEt gives, after hydrolysis and treatment with AcCl, tetraphenylfulgenic anhydride (I), m.p. 267—269°, $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -hexadiene- $\beta\gamma$ -dicarboxylic acid (II), m.p. 194—195.5°, $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -hexatriene- $\beta\gamma$ -dicarboxylic acid (III), m.p. 231—233° (decomp.), and the anhydride (IV), m.p. 222—224°, of the geometrically isomeric acid; the anhydrides of (II) and (III) are hydrolysed during isolation. Their structures point to the intermediate formation of MeCHO from NaOEt. *Me* diphenylitaconate (V), m.p. 94—95° (corresponding *Me* H ester, m.p. 135—138°), condenses with CPh₂ and NaOMe to a product which is hydrolysed and then converted by AcCl into (I) and α -acetoxy- $\alpha\alpha\delta\delta$ -tetraphenyl- Δ^{γ} -butene- $\beta\gamma$ -dicarboxylic acid, m.p. 134—137° (anhydride, m.p. 163—164°), which is partly transformed at 220° into (I) and is decarboxylated in boiling quinoline containing Cu(OAc)₂ to tetraphenylbutadiene. (I) is converted by NaOH followed by acid into tetraphenylfulgenic acid, m.p. 252—255° (red at 240°). (II) is transformed by warm AcCl into its anhydride, m.p. 164—167°, and by boiling quinoline containing Cu(OAc)₂ into $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\gamma}$ -hexadiene, m.p. 196—197°. β -Phenylcinnamaldehyde (2:4-dinitrophenylhydrazones, m.p. 205—206°), (V), and NaOMe give, after hydrolysis and treatment with AcCl, a mixture of (IV) [corresponding acid, m.p. 220—222° (decomp.) after becoming orange-red at 175° and softening at 184°] and (III) (corresponding anhydride, m.p. 212—213°). Hydrolysis of the anhydrides and dehydration of the acids proceeds without apparent inversion but each anhydride gives the same phenylimide, m.p. 234—235°, and each anhydride or acid is transformed by boiling quinoline containing Cu(OAc)₂ into the same $\alpha\alpha\zeta\zeta$ -tetraphenylhexatriene (VI), m.p. 172—174°, isomerised when distilled under diminished pressure to the form, m.p. 203—206°. (VI) is reduced by Na and BuOH to $\alpha\alpha\zeta\zeta$ -tetraphenyl- Δ^{γ} -hexene, m.p. 79—80°, and by H₂ (Pd-BaSO₄) to $\alpha\alpha\zeta\zeta$ -tetraphenylhexane, m.p. 124—125.5°.

H. W.

Pechmann dyes. Scission of *s*-dinaphthyl compounds. P. CHOVIN (Compt. rend., 1938, 207, 1418—1420; cf. A., 1938, II, 333).—The dye (β -C₁₀H₇)₂(C₈H₂O₄) (I), m.p. 361°, with 10% EtOH-KOH at 60° affords (C₁₀H₇)₂(C₈H₄O₆K₂) (II), m.p. 277° (block), which when heated alone or with Ac₂O gives (I). (II) in aq. EtOH changes from red to yellow to give (on acidification) (C₁₀H₇)₂(C₈H₆O₆), m.p. 305°, which when heated alone or with Ac₂O gives a yellow isomeride, m.p. 372°, of (I) with a green fluorescence in C₆H₆.

J. L. D.

cycloHexane series. IV. Isomeric 1-carboxy-4-, -3-, and -2-methylcyclohexane-1-succinic acids. R. D. DESAI, R. F. HUNTER, and G. S. SAHARIA (J.C.S., 1939, 84—86; cf. A., 1937, II, 290; Chatterjee, A., 1937, II, 377).—1-Hydroxy-1-cyano-4-methylcyclohexane and CN-CH₂-CO₂Et in EtOH-NaOEt give Et 1-cyano-4-methylcyclohexane-1-cyanoacetate (not isolated), which with CH₃Br-CO₂Et, first at room temp. and then at 100° (bath), gives Et 1-cyano-4-methylcyclohexane-1- α -cyanosuccinate, m.p. 97° (previous sintering), hydrolysed (conc. H₂SO₄ at room temp., then add H₂O and heat) to the isomeric 1-carboxy-4-methylcyclohexane-1-succinic acids, (A), m.p. 207° [anilide-anilic acid, m.p. 175—

176°; *anil-anilide*, m.p. 187°; *p-methylanil-p-toluidide*, (II), m.p. 186°, and (B), m.p. 178° [also affords (II), probably due to isomerisation at 220°], together with a residue, which is hydrolysed further by conc. HCl to some (A) and a gum. The latter is esterified and alkaline hydrolysis gives (A) and the two 1-carboxy-4-methylcyclohexane-1-acetic acids, m.p. 173° and 137° (cf. A., 1936, 846); an acid (? eutectic mixture), m.p. 188° (previous sintering), from which (A) was obtained with difficulty, was also encountered. Et 1-cyano-3-methylcyclohexane-1-cyanoacetate and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ similarly afford Et 1-cyano-3-methylcyclohexane-1- α -cyanosuccinate, b.p. 208—210°/10 mm., hydrolysed to the isomeric 1-carboxy-3-methylcyclohexane-1-succinic acids, m.p. 210° and 171—172° (each yields the same *p-methylanil-p-toluidide*, m.p. 158—159°). The two isomeric 1-carboxy-3-methylcyclohexane-1-acetic acids, m.p. 163° and 108°, are also isolated. Similarly prepared are Et 1-cyano-2-methylcyclohexane-1- α -cyanosuccinate, b.p. 206—208°/8 mm., and the two isomeric 1-carboxy-2-methylcyclohexane-1-succinic acids, m.p. 195° and 175° [each gives the same *p-methylanil-p-toluidide*, m.p. 172°, and *di-p-toluidide*, m.p. 95° (previous sintering)]. No indication was obtained of isomerism connected with multiplanar forms of the cyclohexane ring. A. T. P.

Arylamino-phthalic acid derivatives. G. J. MARRIOTT and R. ROBINSON (J.C.S., 1939, 134—139).—3-Chlorophthalanil (I), 3-chloro-N-*p-tolyl*- (II), m.p. 160.5°, -*p-anisyl*- (III), m.p. 198°, - β -naphthyl- (IV), m.p. 211°, -*p-nitrophenyl*- (V), m.p. 290° [from $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and 3-chlorophthalic acid or by nitration of (I)] -phthalimides, 3:6- (VI), new m.p. 194°, and 3:4-dichlorophthalanil (VII), new m.p. 179—180°, and 3:6-dichloro-N-*p-tolylphthalimide* (VIII), m.p. 231°, are prepared. (I), NH_2Ph , K_2CO_3 , and Cu-bronze (general method: Frey, A., 1912, i, 477) at 160—170° for 3 hr. give 3-anilinophthalanil, m.p. 144.5—145°, also obtained from (VII) and boiling NH_2Ph (Ullmann). (I) or (II) and $\text{p-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2$ (145—150°) similarly (Frey) give 3-*p-toluidino*-N-*p-tolylphthalimide* (IX), m.p. 152°, and (I) or (III) with $\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ at 160—170° or 145—150° gives 3-*p-anisidino*-N-*p-anisylphthalimide* (X), m.p. 171—172° (note interchange of amine residue on N). (I) and $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ or $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ do not yield cryst. derivatives. (IV) and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ at 145—150° afford 3- β -naphthylamino-N- β -naphthylphthalimide, m.p. 220°, which with $\text{NH}_2\text{Ph}\cdot\text{K}_2\text{CO}_3$ at 170° gives 3- β -naphthylamino-N-phenylphthalimide, m.p. 167°, thus showing reverse displacement of $\beta\text{-C}_{10}\text{H}_7\cdot\text{N}$ by NPh . (VII) and $\text{p-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2$ at 155—160° give 4-chloro-3-*p-toluidino*-N-*p-tolylphthalimide*, m.p. 208—209°, in low yield. (VI) and NH_2Ph at 150—160° (3 hr.), then 135° (20 hr.), give 3:6-dianilinophthalanil, m.p. 197°; $\text{p-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2$ at 167—175° gives 3:6-di-*p-toluidino*-N-*p-tolylphthalimide* (XI), m.p. 164°, and (IX). (VIII) and $\text{p-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2$ at 130—145° for 5 hr. or 220—230° for 2 hr. give 6-chloro-3-*p-toluidino*-N-*p-tolylphthalimide* (XII), m.p. 166—167°, and (XI); none of the latter is obtained without Cu-bronze at 140—150°. Replacement of Cu-bronze- K_2CO_3 by

$\text{Cu} + \text{K acetates}$ at 95—105° (19 hr.) gives [from (VI)] an inseparable mixture, m.p. 181—182° (remelts at 194°), of (VI) and (XII). (VI) and $\text{p-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2 + \text{CuCO}_3$ at 130—140° for 4 hr. gives (IX) and 4:4'-azotoluene, new m.p. 144—145°. (VI) and *p-anisidine* at 150—160° give 3:6-di-*p-anisidino*-N-*p-anisylphthalimide*, m.p. 167—168°. (VI) and $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ at 170—180° afford 3:6-di-, m.p. 302° (decomp.), and at 150—160° give 6-chloro-3-, m.p. 277—278°, -(2'-carboxyanilino)phthalanil. 3-Anilinophthalanil and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ give 3-anilinophthalhydrazide, m.p. 335° (decomp.). Similarly prepared are: 3-*p-toluidino*-, m.p. ~320° (decomp.), 3-*p-anisidino*-, m.p. 320° (decomp.), 3- β -naphthylamino-, m.p. 325° (decomp. >320°), 3:6-dianilinino-, m.p. 276—277°, and 3:6-di-*p-toluidino*-, m.p. ~285° (orange at 120°, blackens at 260°), -phthalhydrazide. Phthal-N-phenylhydrazides are not obtained from (X) and $\text{NH}_2\cdot\text{NHR}$ in $\text{C}_5\text{H}_5\text{N}$. (XI) and P_2S_5 + a trace of NH_2Ph in boiling C_6H_6 give 3:6-di-*p-toluidino*-N-*p-tolylidithiophthalimide*, m.p. 127—128° (softens at 124—125°). (IX) and 70% H_2SO_4 at 160—170° afford 3-methylacridone-6-carboxylic acid, m.p. 302° (decomp.). (X) and its $\beta\text{-C}_{10}\text{H}_7$ analogue do not react with POCl_3 . The auxochromic effect of introducing NHAr in phthalimide is discussed. A. T. P.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. VII. A further resolution of 4:6:4'-trinitrodiphenic acid. D. L. HAMMICK, E. H. REYNOLDS, and G. SIXSMITH (J.C.S., 1939, 98—99; cf. A., 1936, 722).—4:6:4'-Trinitrodiphenic acid is resolved with quinine as described by Christie and Kenner (A., 1926, 408); repeated evaporation of solutions in CHCl_3 gives the cryst. *d*- and *l*-acids. Optically active complexes, $2\text{C}_{14}\text{H}_9\text{O}_{10}\text{N}_3\cdot\text{C}_6\text{H}_6$, are obtained from acids of varying $[\alpha]$ in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ (2:1), from which mixture the Et_2O is carefully distilled until crystallisation begins. The *d*-acid complex has m.p. 176°, and after resolidification, 279—281°, $[\alpha]_{5461}^{20} + 23.14^\circ$ in Et_2O . Repeated crystallisation from $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ (as above) gives acids with $[\alpha]_{5461}^{20} + 47.8^\circ$ and -37.0° in Et_2O (calc. on C_6H_6 -free basis). A. T. P.

5-Halogeno- and 5-hydroxy-trimellitic acids.—See B., 1939, 128.

Oxidation of vitamin-A by the Oppenauer reagent. II. E. HAWORTH, I. M. HEILBRON, W. E. JONES, A. L. MORRISON, and J. B. POLYA (J.C.S., 1939, 128—132).—Vitamin-A, $\text{Al}(\text{O}i\text{Bu})_3$, and COEt_2 (or, less well, COPr^t) (H acceptor) in boiling C_6H_6 and N_2 give the aldehyde (I) (well-defined absorption max. at 4010 Å.) (oxime, m.p. 176—177°; impure semicarbazone, max. at 4030 Å.), which appears to contain an additional double linking situated in the ring (spectrographic evidence discussed); (I) is purified by Girard reagent P. (I) is formed probably through the initial formation of the true vitamin-A aldehyde (the above oxime may be derived from this), which in presence of unreactive COEt_2 is further oxidised in the ring with loss of 2 H. (I) and $\text{Al}(\text{OPr}^t)_3$ in Pr^tOH afford an alcohol, characterised by an absorption max. at 3590 Å. (I) and COMe_2 with $\text{Al}(\text{O}i\text{Bu})_3\cdot\text{C}_6\text{H}_6$ or NaOEt at -5° give a ketone (*p-tolylsemicarbazone*, m.p. 206—207°), not identical

with the ketone, $C_{23}H_{32}O$ (A., 1938, II, 126). The proposed formula

$CH \begin{smallmatrix} \diagup CH_2 \cdot CMe_2 \\ \diagdown CH - CMe \end{smallmatrix} C [CH : CH \cdot CMe : CH]_2 \cdot CHO$ of (I) is supported by ozonolysis, which fails to give geronic acid, but no certain conclusion is reached.

A. T. P.

Action of mixed organomagnesium derivatives on hydroxybenzamides: the phenolic ketones produced. P. L. COUTURIER (Ann. Chim., 1938, [xi], 10, 559—629).—Mainly a detailed account of work already reported (A., 1936, 1107; 1938, II, 98, 361). The following appears new. In hot C_6H_6 and Bu_2O , respectively, hydroxybenzdiethylamides and an excess of $MgEtBr$ give the following yields of hydroxypropionophenones: *o*- 82—84, — (45% in Et_2O), *m*- 10, 70, and *p*-OH 5, 60; 2:4- 10—12, —, and 3:4-(OH)₂ 0, 0, and 3:4:5-(OH)₃ 0, 0%. With acetoxybenzdiethylamides $MgEtBr$ effects decarboxylation (to give $CMeEt_2OH$), but no ketone is formed. Methoxybenz-amides and -diethylamides and $MgEtBr$ give good yields of the ketones (isolated partly as imines if the Mg complex is decomposed with NH_4Cl), but with $MgPhBr$ give NEt_2CPh_2Ar . With $Na-EtOH$ *p*-hydroxy-, m.p. 111°, *p*- and *o*-, m.p. 84°, -methoxypropionophenoxime give respectively α -*p*-hydroxyphenyl- [hydrochloride, decomp. 220—225° (begins at 180°)], α -*p*- and -*o*-anisyl-*n*-propylamine, b.p. 118°/14 mm. (*Bz* derivative, m.p. 144°). *o*- $OMe \cdot C_6H_4 \cdot CO \cdot NEt_2$, m.p. 35°, *p*- $OMe \cdot C_6H_4 \cdot CO \cdot NH_2$, m.p. 161°, 3:4:5-(OMe)₃ $C_6H_2 \cdot CO \cdot NR_2$ ($R = H$, m.p. 176°, and Et , m.p. 54°, b.p. 210°/4 mm.), 3:4-(OMe)₂ $C_6H_3 \cdot CO \cdot NEt_2$, b.p. 210°/18 mm., *p*-anisdiethylamide, m.p. 45°, b.p. 148°/4 mm., γ -diethylamino- γ -*p*-anisyl-*n*-pentane picrate, decomp. ~70—80° (block), diphenyl-*p*-anisylmethyl-diethylamine picrate, decomp. 180—200° (block), and *o*-acetoxypropionophenone, m.p. 26°, b.p. 147°/14 mm., are described. A compound, m.p. 180°, obtained from gallic acid, $COCl_2$, and C_5H_5N , contains Cl and C_5H_5N , and with NH_4Et_2 gives C_5H_5N and NH_4Et_2 gallates.

R. S. C.

γ -Substitution in the resorcinol nucleus. II. Gattermann reaction with resacetophenone. H. A. SHAH and R. C. SHAH (J.C.S., 1939, 132—134; cf. A., 1938, II, 368; 1939, II, 22).—Resacetophenone and $Zn(CN)_2 + KCl$, $AlCl_3$, and HCl in Et_2O or $EtOAc$ at 0° give 2:4-dihydroxy-3-aldehydacetophenone (I), m.p. 112—114° [2:4-dinitrophenylhydrazine, m.p. 283—285° (decomp.); semicarbazone, m.p. 230—231° (decomp.); dioxime, m.p. 218—219° (decomp.)], converted by $CH_2(CO_2Et)_2 +$ piperidine at room temp. into *Et* 5-hydroxy-6-acetylcoumarin-3-carboxylate, m.p. 155—156°. (I) treated successively with aq. $CN \cdot CH_2 \cdot CO_2H \cdot NaOH$ at room temp. and boiling 4% aq. HCl affords 5-hydroxy-6-acetylcoumarin-3-carboxylic acid, m.p. 202—204° (decomp.). (I) and $CH_3Ac \cdot CO_2Et +$ piperidine give 5-hydroxy-3:6-diacetylcoumarin, m.p. 170—171°. (I) is reduced (Clemmensen) to 2-methyl-4-ethylresorcinol, which with $CH_3Ac \cdot CO_2Et$ gives 7-hydroxy-4:8-dimethyl-6-ethylcoumarin, m.p. 187—188°.

A. T. P.

Alkyl ethers of hydroxymethyleneacetophenone. J. WALKER (J.C.S., 1939, 120—122).—Crude

$CHBz \cdot CH \cdot ONa$ and $MeI-EtOH$ or $Me_2SO_4-H_2O$ afford methoxymethyleneacetophenone (I), b.p. 145—147°/12 mm. $CHBz \cdot CH \cdot OEt$ (prep. using EtI) (cf. v. Auwers *et al.*, A., 1925, i, 585) and $CHNa(CO_2Et)_2-EtOH$ at 0° give an unstable product, which when distilled in a vac. loses $EtOH$ to yield *Et* 6-phenyl- α -pyrone-3-carboxylate, m.p. 105—106°, probably identical with the compound, m.p. 107—108°, obtained by Claisen (A., 1904, i, 14). It is probably a precursor of the natural 6-phenylcoumalin, but the latter has not been obtained from it. (I) and $CHNaAc \cdot CO_2Et$ in C_6H_6 at room temp.—100° (bath) give *Et* 3-hydroxydiphenyl-4-carboxylate, m.p. 44—45° [free acid, m.p. 207—208°, decarboxylated at 270° (bath) by quinoline-Cu chromite to 3-hydroxydiphenyl]. A. T. P.

Catalytic dehydrogenation using ordinary or Raney nickel. L. PALFRAY and S. SABETAY (Compt. rend., 1939, 208, 109—112).— β - $C_{10}H_7 \cdot CHMe \cdot OH$ heated in vac. with Ni (much used as a reduction catalyst) affords a considerable proportion of β - $C_{10}H_7 \cdot COMe$. $CHPhMe \cdot OH$ with 5% of Raney Ni at 170—200°/2 hr. affords $PhEt$ and $COPhMe$. Menthol with previously used Ni (Sabatier-Senderens) or Raney Ni at 230° affords 42% and 33% of menthone, respectively. Similarly, cyclohexane-1:4-diol at 250° affords 25% of cyclohexane-1:4-dione. Cu (bronze) is much less efficient than Ni .

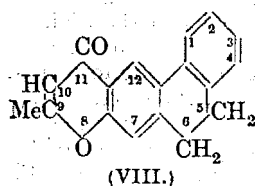
J. L. D.

Stereoisomeric *o*-hydroxybenzophenoximes. A. H. BLATT (J. Amer. Chem. Soc., 1939, 61, 214).— $<0.0001M$ -*syn*-Ph 4-hydroxy-*m*-tolyl ketoxime in Et_2O and saturated aq. $Cu(OAc)_2$ give a ppt. of Cu derivative, but a 0.05M. solution of the *anti*-Ph oxime gives no ppt., thus confirming previous work (A., 1938, II, 101).

R. S. C.

Phenanthrene series. XXIII. Synthesis of acyl compounds derived from 2-hydroxy-9:10-dihydrophenanthrene. E. MOSETTIG and A. H. STUART (J. Amer. Chem. Soc., 1939, 61, 1—7; cf. A., 1939, II, 55).—In the Friedel-Crafts reaction and Fries rearrangement 2-hydroxy-9:10-dihydrophenanthrene (I) behaves mainly, but not entirely, as a Ph_2 derivative. 9:10-Dihydrophenanthrene and H_2SO_4 (2 mols.) at 40° give 50—60% of the 2-sulphonic acid (II) (chloride, m.p. 137°; also obtained less well by $ClSO_3H$ in CCl_4), and a small amount of a (? di)sulphonic acid (chloride, m.p. 240—242°). The Na salt of (II) with KOH at 300° gives 50% of 2-hydroxyphenanthrene. (I) is best (69%) prepared by treating 2-amino-9:10-dihydrophenanthrene successively with $NaNO_2-H_2SO_4-H_2O-C_5H_5N$, $CO(NH_2)_2$, and boiling H_2O . With acyl halides (2.1 mols.) and $AlCl_3$ (2.1 mols.) in $PhNO_2$ at 0—5° (I) gives 7- and 3:7-derivatives in the following yields: 2-hydroxy-7-acetyl- (III) (60—65%), m.p. 190° [*Me* ether (IV), m.p. 134°], -3:7-diacetyl- (V) (15—20%), m.p. 155° [*Me* ether, m.p. 167—168°], -7-propionyl- (40%), m.p. 197—198° [*Me* ether, m.p. 125°], -3:7-dipropionyl- (35—40%), m.p. 129—130° [*Me* ether, m.p. 157°], -7-butyryl- (30%), m.p. 176° [*Me* ether, m.p. 61.5°], and -3:7-dibutyryl- (50%), m.p. 93—94° [*Me* ether, m.p. 102°], -9:10-dihydrophenanthrene. With 1 mol. of $AcCl$ and $AlCl_3$ in $PhNO_2$ (I) gives only 24% of 2-hydroxy-3-acetyl-

9:10-dihydrophenanthrene (VI), m.p. 101° (*Me* ether, m.p. 102°). (V) is obtained in good yield from (VI), but only in poor yield from (III); (VI) may be an intermediate in the reaction with 2 mols. of AcCl . The *Ac* derivative (VII), m.p. 64–65°, of (I) with 2 mols. of AcCl gives (III) and (V). The *Me* ether, m.p. 55°, of (I) with 1 mol. of AcCl gives an inseparable mixture of the 3- and 7-*Ac* derivatives; demethylation (AcOH-HBr) gives small amounts of (III) and (VI). With AlCl_3 , first in CS_2 and then at 140° (no solvent), (VII) gives variable yields (about equal amounts) of (III) and (VI). Structures of the acyl derivatives are proved as follows. The *Me* ethers with NaOCl give 2-methoxy-9:10-dihydrophenanthrene-7-, m.p. 210° (*Me* ester, m.p. 85.5°), and -3-carboxylic, m.p. 163–164° (*Me* ester, m.p. 80–81°), and -3:7-dicarboxylic acid, m.p. 308–309° (*Me_2* ester, m.p. 119°), thus proving their relations to one another. The oxime, m.p. 161°, of (IV) with $\text{HCl-AcOH-Ac}_2\text{O}$ gives 7-acetamido-2-methoxy-9:10-dihydrophenanthrene, m.p. 176.5°, and thence (HCl-AcOH) the amine, m.p. 146°, and (by a diazo-reaction) 2:7-dimethoxy-9:10-dihydrophenanthrene, m.p. 112°, and (by Pd-C at 300°) 2:7-dimethoxyphenanthrene. With *Na* and EtOAc (VI) gives 2-hydroxy-3-acetoacetyl-9:10-dihydrophenanthrene, m.p. 131–132°, which with HCl-AcOH yields 9-methyl-5:6-dihydronaphtho-[1:2-g]chromone (VIII), m.p. 198°, hydrolysed by hot 2*N*- NaOH to 2-hydroxy-9:10-dihydrophenanthrene-3-carboxylic acid (60%), m.p. 219–



220°, and (VI) (15%). Dehydrogenation (Pd-C) of the H_2 -acids affords 2-methoxyphenanthrene-3-, m.p. 213–214° (*Me* ester, m.p. 94–95°), and -7-carboxylic (*Me* ester, m.p. 135°), and -3:7-dicarboxylic acid, m.p. 320–321° (decomp.) (*Me_2* ester, m.p. 161–162°). Most of the OH-ketones described above and earlier (A., 1937, II, 145; 1938, II, 494) have no oestrogenic activity, but the *Ac* derivative, m.p. 99°, of (III) is slightly active.

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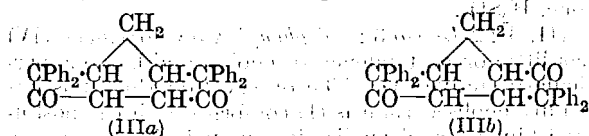
Reactions of aliphatic diazo-compounds with carbonyl derivatives. D. W. ADAMSON and J. KENNER (J.C.S., 1939, 181–189).—Interaction of PhCHO in Et_2O with diazo-ethane (I), *n*-propane, and *n*-butane yields respectively propio-, butyro-, and valero-phenone. (I) and aq. COMe_2 at -10° to 0° yield COMePr^b and $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{OH}$ (as oxide), whilst CH_2BzCl and CH_2N_2 in $\text{MeOH-Et}_2\text{O}$ give α -phenyl- α -chloromethylethylene oxide, b.p. 135–137°/17 mm. Slow addition of $\text{NO-NMe}\cdot\text{CO}_2\text{Et}$ (II) to cyclohexanone (III) in $\text{EtOH} + \text{K}_2\text{CO}_3$ gives suberone and after hydrolysis (0.5% H_2SO_4), 1-hydroxymethylcyclohexanol and impure cyclooctanone, whilst with (I) 2-methylcycloheptanone (IV) [2:4-dinitrophenylhydrazones, m.p. 121–122°; semicarbazone, m.p. 134.5–136° and 177–178.5° (cf. lit.); oxime phenylurethane, new m.p. 125–127°] is formed. *n*-Octylurethane, b.p. 152–155°/19 mm., on nitrosation yields a NO-compound which cannot be distilled, and which with (III) yields 2-*n*-heptylcycloheptanone, b.p. 153–157°/21 mm. (oxime, b.p. 145–

148°/0.8 mm.; 2:4-dinitrophenylhydrazones, m.p. 65°). $\text{Et } \epsilon$ -aminohexanoate is converted by ClCO_2Et into ϵ -carbethoxy-*n*-amylurethane, b.p. 185°/20 mm., the NO-derivative of which with (III) yields 2- ϵ -carbethoxybutylcycloheptanone, b.p. 144–148°/0.7 mm. (oxime, b.p. 169–174°/0.7 mm.), hydrolysed by aq. NaOH to the acid (semicarbazone, m.p. 157–158°). 4-Methylcyclohexanone with (II) and K_2CO_3 in $\text{EtOH-Et}_2\text{O}$ or with $\text{Et}_2\text{O-CH}_2\text{N}_2$ yields 4-methylcycloheptanone, b.p. 84.5°/25 mm., 194.5°/762 mm. (semicarbazone, m.p. 158–160°), and 4-methyl-1-hydroxymethylcyclohexanol; with $\text{NO-NMe}\cdot\text{CO}_2\text{Et}$ (V), or (I) in Et_2O , a ketone, $\text{C}_9\text{H}_{16}\text{O}$, b.p. 204°/757 mm. (semicarbazone, m.p. 162.5–164.5°; 2:4-dinitrophenylhydrazones, m.p. 135–137°; oxime b.p. 132°/23 mm.), results. 3-Methylcyclohexanone with (II) yields 3-methyl-1-hydroxymethylcyclohexanol and a mixture of 3- and 4-methylcycloheptanones, whilst 2-methylcyclohexanone gives 3-methylcycloheptanone, b.p. 188.5–190.5° (semicarbazone, m.p. 179–181°), (IV), methylcyclooctanone, and 2-methyl-1-hydroxymethylcyclohexanol. 4-Ethylcyclohexanone with $\text{MeOH-Et}_2\text{O-CH}_2\text{N}_2$ yields 4-ethylcycloheptanone, b.p. 214–215° (semicarbazone, m.p. 130°), whilst with (I) 2-methyl-4-ethylcycloheptanone, b.p. 102–106°/26 mm., 220–224°/754 mm. (semicarbazone, m.p. 153.5–154.5°; 2:4-dinitrophenylhydrazones, m.p. 100–102°), is formed. 3:5-Dimethylcyclohexanone with (II) or CH_2N_2 yields 3:5-dimethylcycloheptanone, b.p. 88.5–90.5°/23 mm., 205–206°/753 mm. (semicarbazone, m.p. 166.5°), and 3:5-dimethyl-1-hydroxymethylcyclohexanol, m.p. 68–70°, whilst with (V), 2:3:5-trimethylcycloheptanone, b.p. 215°/763 mm. (semicarbazone, m.p. 204–208°; 2:4-dinitrophenylhydrazones, m.p. 91–93°), is formed. 4-Methoxycyclohexanone [2:4-dinitrophenylhydrazones, m.p. 141.5–142.5°; semicarbazone, m.p. 183–185° (lit. 178°)] with (II) gives 4-methoxycycloheptanone, b.p. 111.5–114°/24 mm. (semicarbazone, m.p. 175.5°; 2:4-dinitrophenylhydrazones, m.p. 115–117°), and (probably) 4-methoxy-1-hydroxymethylcyclohexanol. cyclopentanone with (V) or (I) yields a little 2-methylcyclohexanone, and cycloheptanone with (II) gives cyclooctanone (VI) and 1-hydroxymethylcycloheptanol; (VI) does not react with (I) or CH_2N_2 .

J. D. R.

Reaction between diphenylketen and dienes. L. I. SMITH, C. L. AGRE, R. M. LEEKLEY, and W. W. PRICHARD (J. Amer. Chem. Soc., 1939, 61, 7–11).—The structure of the adduct (I) of cyclopentanone and CPh_2CO is proved (cf. Lewis *et al.*, A., 1938, II, 20; Farmer *et al.*, A., 1939, II, 72). (I), obtained in 92% yield in light petroleum, does not react with $\text{NHPh}\cdot\text{NH}_2$ or KMnO_4 in COMe_2 and only slightly with Br-CHCl_3 . With O_3 , followed by CrO_3 , it gives an inipure product, m.p. 77–85° (decomp.), which solidifies at $\sim 111^\circ$ and remelts at $\sim 200^\circ$. With hot NaOH - or KOH-EtOH it yields 2-benzhydryl- Δ^3 -cyclopentene-1-carboxylic acid (II), m.p. 145–147° (cf. Farmer; Staudinger *et al.*, A., 1924, i, 295), oxidised by $\text{KMnO}_4\text{-Na}_2\text{CO}_3$ to 3:4-dihydroxy-2-benzhydrylcyclopentane-1-carboxylic acid (poor yield), m.p. 201.5° (decomp.) (cf. Lewis, *loc. cit.*), and by $\text{O}_3\text{-CrO}_3$ to 8,8-diphenyl-*n*-butane- α,γ -tricarboxylic acid, m.p. 208–209.5° (decomp.). Hydrogenation of

(I) gives 6:6-diphenyldicyclo[0:2:3]heptan-7-one, m.p. 91.5—92.5° (also obtained from cyclopentene and CPh_2CO at 60°), hydrolysed by hot KOH-EtOH to 2-benzhydrylcyclopentane-1-carboxylic acid, m.p. 95—96° (Staudinger, *loc. cit.*, 85°) [anilide, m.p. 142—143° (*loc. cit.*, 139°)], also obtained by hydrogenating (Pt) (II) in Et_2O at 2:3 atm. With CPh_2CO at 110° (I) gives the substance (IIIa or b), m.p. 249—250°, hydrolysed by KOH-EtOH to 3:5- (or 2:5-)dibenzhydrylcyclopentane-1:2- (or -1:3-)dicarboxylic acid, m.p. 140—145°. The adduct, new m.p. 132—133°, from cyclohexene and CPh_2CO with KOH-EtOH



gives 2-benzhydrylhexahydrobenzoic acid, m.p. 153—156°. Interaction of CPh_2CO with cyclohexadiene (1:2 addition; cf. Farmer *et al.*, A., 1938, II, 64), CH_2CPh , and $(\text{CMe}_2\text{CH}_2)_2$, but not with $(\text{CHPhCH}_2)_2$, and failure of keten to react with cyclopentadiene, are reported. R. S. C.

Constitution of eremophilone, hydroxy- and hydroxydihydro-eremophilone. III. A. R. PENFOLD and J. L. SIMONSEN (J.C.S., 1939, 87—89; cf. A., 1938, II, 289).—The constitutions of eremophilone (1-keto-5:10-dimethyl-3-isopropenyl- $\Delta^{8,9}$ -octahydronaphthalene), hydroxy- (1-hydroxy-8-keto-5:10-dimethyl-3-isopropylidene- Δ^1 -octahydronaphthalene), and hydroxydihydro-eremophilone (1-hydroxy-8-keto-4:10-dimethyl-6-isopropenyldecahydronaphthalene) are discussed; they appear to be exceptions to the "isoprene" rule and it cannot be assumed that this rule will apply in the polyterpene series. A possible explanation of the formation of (I) in nature is given. The keto-acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, obtained by ozonolysis of the benzoate of (II), is reduced (Clemmensen) to 1:2-dimethylcyclohexylacetic acid, the Me ester, b.p. 110—112°/19 mm., of which with Se at 360° (24 hr.) affords *o*-xylene, b.p. 135—145°, oxidised by aq. KMnO_4 at 100° (bath) to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Interaction of (II) and alkali H_2O_2 to afford two stereoisomeric $(\text{OH})_2$ -acids is not clear (cf. A., 1933, 71). (II) or (III) and Na-EtOH give 1:8-dihydroxy-4:10-dimethyl-6-isopropyldecahydronaphthalene, oxidised (abnormally) by $\text{Pb}(\text{OAc})_4$ in AcOH to (probably) 88-trimethyl- β -isopropylheptane- α,γ -dicarboxylic acid, m.p. 193—195° (*loc. cit.*). A. T. P.

Action of benzene and aluminium chloride on 2:3-diphenylindone. C. F. KOELSCH (J. Org. Chem., 1938, 3, 456—461).—2:3-Diphenylindone is converted by AlCl_3 (2 mols.) in boiling C_6H_6 into 2:3:3-triphenylhydryndene (I), m.p. 191—193°, also obtained similarly from 2-phenyl-3-*p*-tolylindone. (I) is unaffected by MgPhBr , by Na and BuOH , or by $\text{CrO}_3\text{-AcOH}$ at 50°. (I) and BzCl in $\text{C}_6\text{H}_5\text{N-CHCl}_3$ give 3-benzoyloxy-1:1:2-triphenylhydryndene (II), m.p. 152—154° (corresponding *p*-chlorobenzoate, m.p. 203—204°, and acetate, m.p. 147—148°). CH_2PhCl , (I), and Na in EtOH afford 3-benzoyloxy-1:1:2-triphenylhydryndene, m.p. 149—151°; the Me ether, obtained by use of NaOH and Me_2SO_4 , has m.p. 117—

119°. (II) is oxidised by CrO_3 in AcOH at 60° to 2:3-epoxy-3-benzoyloxy-1:1:2-triphenylhydryndene (III), m.p. 193—195°, reduced by HI in boiling AcOH to BzOH and (I). (III) is hydrolysed (NaOMe-95\% MeOH) (with rearrangement) to 3-hydroxy-1:1:3-triphenylhydrynd-2-one, m.p. 157—159°; reduced by 47% HI in boiling AcOH to 1:3:3-triphenylhydrynd-2-one, m.p. 106—109°, and cleaved by NaOH-EtOH to *o*-benzhydrylbenzoic acid (IV), m.p. 188—189° (decomp.) (Me ester, m.p. 121—123°). This is dehydrated by boiling AcOH containing a little conc. H_2SO_4 to 9:10-diphenyl-9:10-dihydroanthracene-9-carboxylic acid (V), m.p. 236—238° (Me ester, m.p. 195—197°). Oxidation (CrO_3 in AcOH at 80°) of (V) affords 9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene, m.p. 183—185°, reduced by NaI in AcOH to 9:10-diphenylanthracene. (IV) is oxidised to *o*-benzhydrylbenzophenone, m.p. 84—86°, whence (MgPhBr) *o*-benzhydryltriphenylcarbinol, m.p. 213—215°, dehydrated to 9:9:10-triphenyl-9:10-dihydroanthracene, m.p. 223—225°. H. W.

Action of aluminium chloride on certain phenylated fulgenic anhydrides. C. F. KOELSCH and H. J. RICHTER (J. Org. Chem., 1938, 3, 465—472).—Tetraphenylfulgenic anhydride (I) is converted by AlCl_3 in C_6H_6 into 1:2:3:4-dibenzoylencnaphthalene (II), m.p. (block) 308—310°, and 2-phenyl-3:4-benzofluorenone-1-carboxylic acid (III), m.p. (block) 264—266°. (II) is a secondary product formed by dehydration of (III). In boiling quinoline containing a little $\text{Cu}(\text{OAc})_2$ (III) passes into 2-phenyl-3:4-benzofluorenone, m.p. 191°. (III) is obtained synthetically from 1:4-diphenylnaphthalene-2:3-dicarboxylic anhydride, new m.p. 288—289°, C_6H_6 and AlCl_3 . Triphenylfulgenic anhydride (IV), AlCl_3 , and C_6H_6 give 3:4-benzofluorenone-1-carboxylic acid, m.p. (block) 283—286° (Me ester, m.p. 148—150°), decarboxylated to 3:4-benzofluorenone, m.p. 161—162° (oxime, m.p. 213—215°). (I) is converted by AlCl_3 in PhNO_2 at 60° into 3-phenyl-2- α -carboxy- $\beta\beta$ -diphenylvinylindone (V), m.p. 237—241°, decarboxylated to 3-phenyl-2- $\beta\beta$ -diphenylvinylindone, m.p. 147—148°, and transformed by AlCl_3 in boiling C_6H_6 into (III) in almost quant. yield. (V) is converted by SOCl_2 into its chloride, m.p. 183—186°, which affords (II) when boiled with AlCl_3 in C_6H_6 and gives an unidentified compound, m.p. 161—163°, when treated with AlCl_3 in PhNO_2 . (IV) and AlCl_3 in PhNO_2 yield 3-phenyl-2- α -carboxystyrylindone, m.p. 196—199°, decarboxylated to 3-phenyl-2-styrylindone, m.p. 144—146°. $\alpha\alpha\zeta$ -Tetraphenylhexatriene- $\beta\gamma$ -dicarboxylic anhydride, m.p. 222—224°, AlCl_3 , and PhNO_2 give 88-diphenyl- α -3-phenyl-2-indonyl- $\Delta^{\alpha\gamma}$ -pentadienoic acid, m.p. 242—246°, softens at 235°, also obtained from the isomeric anhydride, m.p. 212—214°; it is decarboxylated to 88-diphenyl- α -3-phenyl-2-indonylbutadiene, m.p. 165—167°. A mechanism for the conversion of (I) into (III) is given. (I) could not be converted into 3:3'-diphenyl-2:2'-di-indonyl. H. W.

periNaphthindene series. III. Action of magnesium phenyl bromide on 7-ethoxyperi-

naphthinden-9-one. C. F. KOELSCH and R. H. ROSENWALD (J. Org. Chem., 1938, 3, 462—464; cf. A., 1938, II, 19).—Contrary to Calderaro (A., 1914, i, 41), 7-ethoxyperinaphthinden-9-one reacts with MgPhBr by 1:4 addition giving 7-ethoxy-1-phenyl-1:9a-dihydroperinaphthinden-9-one (I), m.p. 156—157°, hydrolysed (HBr in boiling AcOH) to 1-phenyl-1:9a-dihydroperinaphthindane-7:9-dione, m.p. 250° when brought into a bath preheated to 240°. The position of Ph is shown by converting (I) by *p*-benzoquinone in C₆H₆ into 7-ethoxy-1-phenylperinaphthinden-9-one, m.p. 153—154°, hydrolysed to 1-phenylperinaphthindane-7:9-dione, m.p. 240—250° (decomp.), oxidised (KMnO₄) to 2-phenylnaphthalic anhydride, m.p. 239—240°. H. W.

Reactions and enolisation of cyclic diketones.

IV. 1:2-Diketo-3:4:5-triphenylcyclopentene. C. F. KOELSCH and T. A. GEISSMAN. **III. 1:2-Diketo-3:4-diphenylcyclopentene.** T. A. GEISSMAN and C. F. KOELSCH (J. Org. Chem., 1938, 3, 480—488, 489—502).—IV. The ketonic nature of 1:2-diketo-3:4:5-triphenyl-Δ³-cyclopentene (I) is in agreement with the postulated hindrance of enolisation by the presence of a double linking in a five-membered ring. 3-Hydroxy-3:4:5-triphenyl-Δ⁴-cyclopentenone, m.p. 164—165° (cf. Dilthey and Hurtig, A., 1935, 204) [phenylhydrazone, m.p. 173—174° (decomp.); *p*-nitrophenylhydrazone, m.p. 214—215° (decomp.); CHPh derivative, m.p. 217.5—218°], is converted by 45% HI in boiling AcOH into 3:4:5-triphenyl-Δ³-cyclopentenone, m.p. 142—143°, the 2-oximino-derivative, m.p. 228—229° (decomp.) (benzoate, m.p. 154—155°), of which is converted by CH₂O and conc. HCl in boiling AcOH into (I), m.p. 162—163.5°, with a by-product, m.p. 235° (decomp.). (I) is not sol. in dil. aq. alkali but gives in NaOMe-MeOH a dark blue-green colour which fades to yellow after several hr. at room temp. It shows no tendency to form an acetal. With *o*-C₆H₄(NH₂)₂ it affords a phenazine, C₂₉H₂₀N₂, m.p. 226—227° (decomp.). The possibility of its enolisation is established by its conversion by BzCl in C₆H₅N into 2-keto-3:4:5-triphenyl-Δ^{3:5}-cyclopentadienyl benzoate, m.p. 242—243° (decomp.). The diketonic structure of (I) is established by its conversion by MgPhBr into 1:2:3:4:5-pentaphenyl-Δ³-cyclopentadiene-1:2-diol, the identity of which is proved by its conversion (HI) into pentaphenylcyclopentadiene, new m.p. 252—254°. (I) is cleaved by H₂O₂-NaOH to αβγ-triphenylglutaconic anhydride (II), m.p. 166—167°. Br in AcOH at 65° converts (I) into 5-bromo-3:4:5-triphenyl-Δ³-cyclopentene-1:2-dione (III), m.p. 145—146°, transformed by boiling dil. AcOH into (II) and converted by boiling MeOH into 5-methoxy-3:4:5-triphenyl-Δ³-cyclopentene-1:2-dione, m.p. 148—150° (corresponding phenazine, m.p. 200—201°), which is cleaved (H₂O₂-NaOH) to α-methoxy-αβγ-triphenylglutaconic anhydride, m.p. 161—162° (decomp.). MgPhBr and (III) afford 2-hydroxy-2:3:4:5-tetraphenyl-Δ³-cyclopentenone, m.p. 208.5—210°, converted by warming with AcOH containing a little H₂SO₄ or by distillation under reduced pressure into tetraphenylcyclopentadienone, m.p. 217—218°, by boiling AcOH-HI into tetraphenylcyclopentenone,

m.p. 162—163°, and by AcOH-HCl-Zn into tetraphenylcyclopentenol, m.p. 174—176°. With AgOAc in AcOH (III) rapidly yields AgBr and the compound, $\text{CPh}(\text{OAc})\text{CO} > \text{CO}$ or $\text{CPh} \begin{smallmatrix} \text{C}(\text{OAc})\text{O} \\ \diagup \quad \diagdown \\ \text{CPh} = \text{CPh} \end{smallmatrix} > \text{CO}$, m.p. 174—177°, converted by conc. H₂SO₄ into 3-hydroxy-4-phenyl-1:2-benzofluorenone, m.p. 237—238°, also obtained from (II) and conc. H₂SO₄. Conc. H₂SO₄ converts (III) into (?) -bromo-3-hydroxy-4-phenyl-1:2-benzofluorenone, m.p. 287—289° (benzoate, m.p. 240—241°), also obtained by addition of a slight excess of Br in AcOH to a solution of (II) in conc. H₂SO₄.

III. 1:2-Diketo-3:4-diphenyl-Δ³-cyclopentene (IV) has little or no tendency to enolise and has one particularly active CO. The observation that it is less readily enolised than is (I) conforms with the postulated hindrance of enolisation in such diketones by a second H attached to C bearing H involved in enolisation. 3:4-Diphenyl-Δ³-cyclopentenone (improved prep.) is converted by Bu nitride and conc. HCl in EtOH at 50—55° into 2-oximino-3:4-diphenyl-Δ³-cyclopentenone, m.p. 223—224° (decomp.) [benzoate, m.p. 142—143° (decomp.)], transformed by CH₂O-HCl-AcOH into (IV), m.p. 178—182° or 186—188° (slow decomp.) [possibly dimorphous forms], which gives a phenazine C₂₃H₁₆N₂, m.p. 236—237°, and the 1-oxime, m.p. 237—239° (decomp.) after darkening at 215°. (IV) is cleaved by NaOH-H₂O₂ to αβ-diphenylglutaconic anhydride (V), m.p. 126—127° or [+(?) C₆H₅], m.p. 111—112°. When boiled with 10% NaOH, dil. HCl, or AcOH containing P and I (IV) gives an αβ-diphenylglutaconic acid, m.p. 165—166° (decomp.), re-converted into (V) by distillation under 20 mm.; an isomeric acid, m.p. 204—205°, is obtained when (V) is boiled with Zn dust and 10% NaOH for 1 hr. Distillation of the dry Na salt derived from (V) with soda-lime affords α-methylstilbene, m.p. 80—81.5°. 3-Hydroxy-1:2-benzofluorenone, m.p. (block) 307—308° (benzoate, m.p. 235—236°), is obtained from (V) and conc. H₂SO₄. MgPhBr converts (IV) in C₆H₆ into 1:2:3:4-tetraphenyl-Δ³-cyclopentene-1:2-diol (VI), m.p. 200—201°, converted by boiling MeOH containing a little H₂SO₄ into 1-methoxy-1:2:3:5-tetraphenylcyclopentadiene, m.p. 150—151°, and by boiling AcOH containing a little conc. H₂SO₄ into 2:3:4:5-tetraphenylcyclopentadienone, m.p. 216—218°. Oxidation of (VI) with Pb(OAc)₄ leads to αβγε-tetraphenyl-Δ⁸-pentene-αε-dione, m.p. 110—112° (Fe^{III} derivative, m.p. 187—188°). With the requisite proportion of Br in boiling AcOH (IV) gives 5-bromo-3:4-diphenyl-Δ³-cyclopentene-1:2-dione, m.p. 181—182.5° (decomp.), which does not afford cryst. products with MeOH, NaOMe-MeOH, NaOAc in AcOH, or MgPhBr. With a larger proportion of Br (IV) yields 5:5-dibromo-3:4-diphenyl-Δ³-cyclopentene-1:2-dione, m.p. 162—165°, decomp. ~185°, which does not yield a cryst. product with MeOH and gives NH₂Ph.HBr and a non-cryst. red oil with NH₂Ph. With NH₂Ph or *p*-C₆H₄Me.NH₂ in boiling C₆H₆ (IV) gives substances, m.p. 81—83° and 87.5—89°, respectively. With NH₂Ph in cold Et₂O (IV) affords the unstable 1-anilino-1-hydroxy-2-keto-3:4-diphenyl-Δ³-cyclopentene, m.p. 108—

110° (decomp.), which regenerates (IV) when treated with dil. HCl; the analogous 1-*p*-toluidino-compound has m.p. 120—122° (decomp.). (IV) is converted by boiling MeOH containing a little conc. HCl into 1:1-dimethoxy-3:4-diphenyl- Δ^3 -cyclopenten-2-one, m.p. 120—121°, from which (IV) is re-formed by boiling AcOH containing a drop of HCl; it is converted by MgPhBr into 1:1-dimethoxy-2:3:4-triphenyl- Δ^3 -cyclopenten-2-ol, m.p. 124—125°, transformed into a dimeride, m.p. 257—258° (darkening), of 2:3:4-triphenylcyclopentadienone by boiling AcOH containing 2% of H₂SO₄. H. W.

Enolisation of 1:2-diketohydrindene and of 1:2-diketo-3-phenylhydrindene. C. F. KOELSCH and H. HOCHMAN (J. Org. Chem., 1938, 3, 503—505).—The ultra-violet absorption of 1:2-diketo-3-phenylhydrindene indicates that it exists in the enolic form whilst that of 1:2-diketohydrindene (I) shows that this compound is ketonic. The chemical behaviours of these substances are consistent with these structures. (I) can be boiled with Br in AcOH without change but in the presence of NaOAc or HBr it yields 3:3-dibromo-1:2-diketohydrindene, m.p. 141—142°. H. W.

2-Oximino- or 2-nitroso-indane-1:3-dione? G. WANAG and A. LODE (Ber., 1939, 72, [B], 49—51).—The product (I) of the action of HNO₂ on indane-1:3-dione is oxidised by HNO₃ (*d* 1.4) in AcOH to 2-nitroindane-1:3-dione (II) (+2H₂O), m.p. 115°, also obtained by action of N oxides on indanedione (III) in AcOH or as Na salt from (III) and NaNO₂ in AcOH. (II) is reduced by boiling HCO₂H to (I), m.p. 210—212° when rapidly heated (cf. Teeters *et al.*, A., 1933, 953). (I) and Br in boiling CHCl₃ afford 2:2-dibromointhane-1:3-dione, m.p. 178°, bromonitrosoindanedione being probably formed intermediately. (I) gives a red solution in alkali hydroxide, probably owing to enolisation. (I) must therefore be regarded as 2-nitrosoindane-1:3-dione rather than as 2-oximinointhane-1:3-dione. In contrast with (II), characteristic ppts. are not formed from (I) and certain inorg. cations and org. bases. The ninhydrin reaction is observed when (I) and aq. α -NH₂-acids are subjected to protracted heating. H. W.

Photochemistry of Δ^4 -cholestenone. E. BERGMANN and Y. HIRSBERG (Nature, 1938, 142, 1037—1038).—Irradiation (Hg arc) of a 5% solution of Δ^4 -cholestenone in C₆H₁₄ or C₆H₆ immediately produces an insol. cryst. substance (I), C₄₂H₆₂O₂, m.p. >360°, by loss of 6 C and subsequent dimerisation. (I) is also accompanied by a resinous product. When O₂ is not rigidly excluded, cholestane-3:4-dione, new m.p. 157° (quinoxaline, new m.p. 228°), is also formed through photo-oxidation. Cholesteryl acetate is mainly resinsified on irradiation; vac. distillation then gives (in some cases) Δ^3 : Δ^5 -cholestadiene. L. S. T.

Cholestenone pinacone and its thermal decomposition. F. GALINOVSKI and H. BRETSCHNEIDER (Monatsh., 1938, 72, 190—196).—Windaus' cholestenone pinacone, m.p. 229—230°, [α]_D²⁵ +93.1° in CHCl₃ (cf. A., 1906, i, 174), is the bimol. 3:3' compound, since it has 2 active H, is unchanged by

Ac₂O—C₅H₅N—CHCl₃, is oxidised by Pb(OAc)₄ to cholestone (1), is hydrogenated (Pd-black) in EtOH with loss of 2H₂O to an unsaturated [C(NO₂)₄] hydrocarbon, C₅₄H₉₀, and, when heated at 0.01 mm., gives cholestanone and (1). R. S. C.

Action of enol esters of testosterone. K. MIESCHER, W. H. FISCHER, and E. TSCHOPP (Biochem. Z., 1938, 300, 14—27; cf. A., 1938, III, 807, 908).—Partly a more detailed account of work previously reviewed (A., 1937, III, 492). The following enol esters of testosterone are described: 3-acetate 17-propionate, m.p. 140—141°, 3-acetate 17-n-butyrate (1), m.p. 96.5—98°, 3-acetate 17-isobutyrate, m.p. 134—136°, 17-acetate 3-propionate, m.p. 139.5—141°, 3-propionate 17-isobutyrate, m.p. 133.5—135°, 17-acetate 3-n-butyrate, m.p. 97—99°, 17-propionate 3-n-butyrate, m.p. 79—80°, 3-benzoate 17-acetate, m.p. 192—193°. J. N. A.

Preparation of a pregnane compound from dehydroandrosterone. H. E. STAVELY (J. Amer. Chem. Soc., 1939, 61, 79—80).—17-Acetylenyl- Δ^5 -androstene-3:17-diol (prep. in 80—85% yield from dehydroandrosterone by C₂H₂ and CMe₂Et-OK in CMe₃Et-OH—Et₂O—C₆H₆ at room temp.), m.p. 240—242°, [α]_D²⁵ —119° in CHCl₃, with HgSO₄ in H₂O at 110—120° gives 10% of Δ^5 -pregnene-3:17-diol-20-one (1), m.p. 276—278°, [α]_D²⁵ —106° in dioxan (oxime, m.p. 245—246°) (cf. Ruzicka *et al.*, A., 1939, II, 76), and a (?) Hg compound, which with NaOH—H₂S gives a further 20% of (1). Attempts to add MeOH gave only mixtures. R. S. C.

3:7:12-Trihydroxypregnan-20-one.—See B., 1939, 216.

Isolation of a keto-lactone from the urine of pregnant mares. J. D. JACOBS and E. LAQUEUR (Rec. trav. chim., 1939, 58, 77—82).—The ketone in the non-phenolic extract of this urine (cf. Heard, A., 1938, II, 146) is a saturated keto-lactone (I), C₁₉H₂₈O₃, m.p. 258° [semicarbazone, m.p. ~310° (decomp.)], unaffected by Ac₂O, Na—Hg, CrO₃—AcOH, or Br; it gives no pure oxime, and has no oestrogenic or comb.-growth-promoting effect. When boiled with 2N-EtOH—KOH, (1) gives a OH-acid, C₁₉H₂₈O₄, m.p. 240—243°. The data of Marker *et al.* (A., 1938, II, 369) on (1) are criticised. E. W. W.

Synthesis of sexual hormone glycuronides. E. SCHAPIRO (Nature, 1938, 142, 1036).—Me α -tri-acetylbromoglycuronate with dehydroandrosterone and α -oestradiol benzoate in C₆H₆ + Ag₂CO₃ gives the corresponding acetylated glycuronides (formulae given), m.p. 194—196°, [α]_D²⁵ —8.4° in CHCl₃, and m.p. 189—191°, [α]_D²⁵ \pm 0°, respectively, hydrolysed (loss of acyl and Me) by MeOH—Ba(OH)₂ to dehydroandrosteroneglycuronide, m.p. 262—264° (decomp.), and oestradiol-17-glycuronide, m.p. 191—194° (decomp.; previous shrinking), respectively (first isolated as Ba salts), which are less active than the uncoupled hormones. L. S. T.

Conversion of dehydroandrosterone into progesterone; simple artificial preparation of the hormone of pregnancy from cholesterol. A. BUTENANDT and J. SCHMIDT-THOMÉ (Ber., 1939, 72,

[B], 182—187).—In extension and amplification of work already reviewed (A., 1938, II, 236), $\Delta^{5,16}$ -pregnadien-3-ol-20-one (I), new m.p. 216° (acetate, m.p. 176° , $[\alpha]_D^{20} -33.4^\circ$ in EtOH), is oxidised by $\text{Al}(\text{OPr}^i)_3$ in presence of PhMe and cyclohexanone to 16-dehydropregesterone, m.p. 186—188°, which is devoid of oestrogenic properties. (I) is readily partly hydrogenated (Raney Ni) to Δ^5 -pregnen-3-ol-20-one which is converted by known methods into progesterone. 17-Cyano-3-acetoxy- $\Delta^{5,16}$ -androstadiene (II) (*loc. cit.*) is hydrolysed to 17-cyano- $\Delta^{5,16}$ -androstadien-3-ol, m.p. 176° , also obtained by the restricted action of MgMeBr on (II). H. W.

1:4-Dihydroxy-2-acetylanthraquinone. H. WILLSTAEDT and M. MICHAELIS (Svensk Kem. Tidsskr., 1938, 50, 274—278).—Quinacetophenone, $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, H_3BO_3 , and conc. H_2SO_4 at $150\text{--}160^\circ$ and then at $190\text{--}200^\circ$ give 1:4-dihydroxy-2-acetylanthraquinone (I), m.p. $199\text{--}200^\circ$, in very small yield. (I) does not depress the m.p. of quinizarin (II). (I) is transformed by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ and Na_2CO_3 in $p\text{-C}_6\text{H}_4\text{Cl}_2$ at 170° into 1:4-dimethoxy-2-acetylanthraquinone, m.p. 171° , which does not depress the m.p. of 1:4-dimethoxyanthraquinone. (II) cannot be chromatographically separated from its 2-Ac derivative by CaCO_3 or from its Me ether by Al_2O_3 . The Me_2 ethers of (II) and alizarin are readily separable by Al_2O_3 . Condensation of acetoveratrone, $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, H_3BO_3 , and conc. H_2SO_4 gives alizarin Me_2 ether. H. W.

Halogenoanthraquinone- β -carboxylic acids.—See B., 1939, 128.

Diaminodiphenoxyanthraquinonedisulphonic acids.—See B., 1939, 128.

Walden inversion. III. Reaction of sulphonic esters with alcohols. W. HÜCKEL and W. TAPPE (Annalen, 1939, 537, 113—131; cf. A., 1938, II, 315).—Menthyl p -toluenesulphonate (I) in boiling cyclohexane decomposes completely into dl -menthene (II) and high-boiling products; this is due to traces of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ formed, as CaCO_3 stabilises the ester and the small amount of decomp. occurring in its presence yields d -(II). When distilled in steam, (I) gives much (II) and some l -menthol (III); in presence of CaCO_3 much less (II) and neomenthol (IV) are formed. In boiling EtOH (I) gives much (II), $\alpha_D +34^\circ$, and some of the Et ethers of l -(III) and d -(IV); in presence of CaCO_3 less (II), $\alpha_D +78^\circ$, much of the Et ether of d -(IV), and less of the Et ether of l -(III), (III), and (IV) are formed. NaOEt does not affect (I) in PhMe or Et_2O ; in EtOH it gives (II) and a little l -(III) and its Et ether. (I) decomposes less fast in MeOH or Pr^iOH than in EtOH, and the products are similar but differ in relative amounts. Menthyl benzenesulphonate behaves similarly. The p -toluenesulphonate of *trans*-decahydro- β -naphthol (V), m.p. 75° , with CaCO_3 in EtOH gives about 40% of octahydronaphthalene (VI), 60% of Et ether [80% thereof from *trans*-decahydro- β -naphthol (VII), m.p. 53°], and a little free (VII). The p -toluenesulphonate of (VII) similarly gives 65% of (VI), about 35% of Et ether [90% thereof from (V)], and a

little (V). Reaction mechanisms and the homogeneity of (II) are discussed. R. S. C.

Organic sulphur compounds. IV. Action of hydrocyanic acid, ammonia, and hydrogen sulphide on carvone. K. ABER (Sci. Rep. Tokyo Bunrika Daigaku, 1938, A, 3, 217—230; cf. A., 1936, 212).—Carvone treated with KCN (2 mols.) in aq. EtOH, then made slightly acid, kept, and finally treated with NH_3 and H_2S gives 2-amino-2:6-dicyano- Δ^8 - p -menthene (I), m.p. 129.5° [hydrochloride, m.p. $>225^\circ$; converted by H_2O into 6-cyanodihydrocarvone (II), m.p. $93.5\text{--}94.5^\circ$], and dihydrothiocarvone-6-carboxythioamide (III), m.p. $198\text{--}199^\circ$. If 1 mol. of KCN or, better, NaCN is used, 2-imino- Δ^8 - p -menthene-6-carboxythioamide (IV), m.p. $151\text{--}152^\circ$ (platinichloride), and, sometimes, a substance (C 59.3, H 8.4, N 14.8, S 14.7%), m.p. $149\text{--}150^\circ$, are obtained. The hydrochloride, m.p. $165\text{--}166^\circ$, of (IV) in hot H_2O gives dihydrocarvone-6-carboxythioamide, m.p. 133° , hydrolysed by hot 10% HCl to β -dihydrocarvone-6-carboxylic acid (Lapworth, J.C.S., 1906, 89, 963). By $\text{KCN}\text{--}\text{NH}_3\text{--}\text{H}_2\text{S}$ treatment (II) gives (III) and by $\text{NH}_3\text{--}\text{H}_2\text{S}$ in EtOH yields (IV) and its H sulphide (V), m.p. $171\text{--}172^\circ$ (converted by hot, dil. HCl into a substance, $\text{C}_{11}\text{H}_{18}\text{O}_3\text{S}$, m.p. 138°). With $\text{NH}_3\text{--}\text{H}_2\text{S}$ in EtOH 6-cyanodihydrocarvone cyanohydrin, m.p. variable, $104\text{--}108^\circ$ and $134\text{--}135^\circ$ (*loc. cit.*, p. 1819), or (I) gives (III) and (IV), but (IV) gives only (V). With H_2S in EtOH (II) gives a substance, $\text{C}_{11}\text{H}_{17}\text{NS}_2$, m.p. $80\text{--}81^\circ$ [possibly an isomeride of (III); also obtained from (I)], and a substance, $\text{C}_{11}\text{H}_{17}\text{ONS}$, $1.5\text{H}_2\text{S}$, m.p. $219\text{--}220^\circ$.

R. S. C.

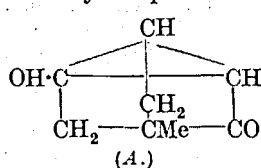
Complexes of magnesium bromide with terpene ketones and alcohols. G. V. TSCHELINCEVA (J. Gen. Chem. Russ., 1938, 8, 588—591).— $\text{MgBr}_2\cdot 3\text{Et}_2\text{O}$ in Et_2O and camphor yield the complexes $\text{MgBr}_2\cdot 2\text{C}_{10}\text{H}_{16}\text{O}$ (I) and $\text{MgBr}_2\cdot 3\text{C}_{10}\text{H}_{16}\text{O}$ (I) and borneol in Et_2O give $\text{MgBr}_2\cdot 2\text{C}_{10}\text{H}_{16}\text{O}\cdot 2\text{C}_{10}\text{H}_{17}\text{OH}$; this with EtOH or $iso\text{-C}_5\text{H}_{11}\cdot\text{OH}$ gives oily products, with Pr^iOH give $\text{MgBr}_2\cdot 2\text{C}_{10}\text{H}_{16}\text{O}\cdot \text{Pr}^i\text{OH}$, and with PhOH gives $\text{MgBr}_2\cdot 2\text{C}_{10}\text{H}_{16}\text{O}\cdot \text{PhOH}$. R. T.

Camphor series. V. Some derivatives of oximinothiocabphor. D. C. SEX (J. Indian Chem. Soc., 1938, 15, 537—542; cf. A., 1936, II, 856).—The formation of oximinothiocabphor (I) (Bz derivative, m.p. $115\text{--}116^\circ$) from $iso\text{-C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$ and Na thiocabphor involves a migration of NO from S to C. (I) can act as the thiol, $\text{C}_8\text{H}_{14}\text{--}\text{C}(\text{NO})\text{--SH}$ or the thio-ketone, $\text{CS}\text{--}\text{C}(\text{NO})\text{--OH}$. dl -(I) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in NaOH or NaOAc or $\text{C}_5\text{H}_5\text{N}$ afford α -(II), m.p. 201° , and β -camphorquinonediaxime (III), m.p. 248° , and bornylene- dl -1:2:5-thiodiazole (IV), m.p. 218° , $\text{C}_8\text{H}_{14}\text{--}\text{C}(\text{N})\text{--N}\text{--S}$. l -(I) similarly gives (II), (III), and α -bornylene-1:2:5-thiodiazole, m.p. 221° , $[\alpha]_D^{24} +75.27^\circ$ in EtOH. (IV) is also obtained from (II) and $\text{H}_2\text{S}\text{--}\text{EtOH}\text{--}\text{NaOAc}$, and is reduced by $\text{Zn}\text{--}\text{AcOH}$ at 100° (bath) to bornylenediamine (dihydrochloride, m.p. $287\text{--}288^\circ$). (I) and MgMeI afford (3) the anhydride of oximinomethylthioborneol,

$C_8H_{14} \begin{smallmatrix} C=N \\ \diagup \diagdown \\ CMe-S \end{smallmatrix}$, b.p. 105–106°/6 mm. (I) and MeI–NaOEt at 80° give *S*-methylmitrosothiocamphor, $C_8H_{14} \begin{smallmatrix} C=NO \\ \diagup \diagdown \\ C-SMe \end{smallmatrix}$, b.p. 95–96°/6 mm., hydrolysed by dil. HCl (1 : 1) to MeSH and oximinocamphor, m.p. 152°. (I), CH_2O , and a little H_2SO_4 , then fuming HCl, at 100° (bath), afford camphorquinone, m.p. 198°, and a little monothiocamphorquinone, m.p. 196° [NH_2OH gives H_2S and (III)] (cf. Lapworth, J.C.S., 1907, 91, 1134). During the prep. of (I) (*loc. cit.*), an *isomeride*, b.p. 105–106°/5 mm., is isolated in small yield. Solid *L*-(I) is pink, but dissolves in org. solvents with a blue colour. The blue EtOH solution, rapidly cooled, gives prismatic crystals, but slow cooling gives octahedra. *dl*-(I) is blue in solid and solution. Absorption spectra are recorded.

A. T. P.

Degradation of dimethylcamphor in the animal organism. Biological oxidation of methyl groups in terpenes. F. REINARTZ and K. MEESSEN (Ber., 1939, 72, [B], 1–7).—If dimethylcamphor is administered to a dog, the Me attached to C_{13} are by far the most readily hydroxylated since 3-methylcamphorcarboxylic acid, m.p. 98–100.5° (decomp.) [*Me* ester, m.p. 87° (corr.)], is isolable in considerable amount. When melted it gives CO_2 and 3-methylcamphor. The main component of the



degradation products is 4-hydroxydimethylcamphor [*p*-nitrobenzoate, m.p. 178.4–180.4° (corr.)]. Small amounts of camphoric acid and anhydride are also obtained, probably due to the oxidation of both Me groups at C_{13} . The oxidation of camphor to the substance A, m.p. 137–138.5° (monosemicarbazone), is described.

H. W.

Fenchene series. IX. Stereoisomeric *dl*- β -fenchocamphorols. G. KOMPPA and S. BECKMANN (Annalen, 1939, 537, 140–143; cf. A., 1938, II, 371).— β -Fenchocamphorol, m.p. 44–45° (A., 1936, 729), is resolved into β -fenchocamphorol (mainly), m.p. 64–65°, b.p. 198–199° (*H* phthalate, m.p. 126–127°; phenylurethane, m.p. 96–97°), and iso- β -fenchocamphorol, m.p. 60–61° (*H* phthalate, m.p. 130–131°).

R. S. C.

*epi-iso*Fenchone. G. A. NYMAN (Annalen, 1939, 537, 131–139).—The Na derivative (prep. by $NaNH_2$ in C_6H_6 or Et_2O) of *dl*-isofenchone (I) with CO_2 in C_6H_6 gives a 70% yield of *dl*-isofenchone-3-carboxylic acid (II), m.p. 114°, the reaction being sterically homogeneous owing to the proximity in space of C_{13} and one of the *gem*-Me. When kept alone, (II) gives (I), and with NH_2OH or $NH_2CO \cdot NH \cdot NH_2$ in EtOH (II) gives CO_2 and the CO-derivatives of (I). Electrolytic reduction of (II) in aq. K_2CO_3 gives homogeneous *dl*-isofenchone-3-carboxylic acid (III), m.p. 137–139°, converted by AcCl and distillation of the resulting acetate at 16 mm. into δ -fenchene-3-carboxylic anhydride, m.p. 133–135°, and thence into the corresponding acid (IV), m.p. 139–140°, the structure of which is proved by oxidation by $KMnO_4$ to *dl*-isofenchocamphoric

acid (V) and (III). With $SOCl_2$ (IV) gives the chloride, b.p. 112°/17 mm. (converted on storage into HCl and a substance, m.p. 133–135°), which gives the azide and thence by hot, conc. HCl *dl*-*epi*-isofenchone, b.p. 195–198° [gives no semicarbazone; *oxime*, m.p. 64–65° (*Bz* derivative, m.p. 86–87.5°)], oxidised to (V).

R. S. C.

1-Methylsantene oxide and methylsantene glycol. G. KOMPPA and G. A. NYMAN (Ber., 1939, 72, [B], 16–18; cf. A., 1935, 865).—1-Methylsantene is smoothly transformed by BzO_2H in $CHCl_3$ at 0° into 1-methylsantene oxide (I), b.p. 57.5–58°/7.5 mm., hydrated by 10% H_2SO_4 at 0° to methylsantene glycol [2 : 3-dihydroxy-1-methyl-2 : 3-dihydrosantene] (II), m.p. 197–198°. Oxidation of (II) with NaOBr yields 1-methylcyclopropane-1 : 3-dicarboxylic acid in very small amount. When (I) is distilled with SiO_2 gel at atm. pressure or when (I) or (II) is distilled in vac. an unidentified compound, b.p. 215–216°, results. This gives a strong aldehyde reaction with magenta- H_2SO_3 but only slowly reduces Ag_2O . It gives an intense colour with $C(NO_2)_4$ and strongly reduces $KMnO_4$. It yields a semicarbazone, $C_{11}H_{19}ON_3$, m.p. 179–180°. It appears to be monocyclic but is not fenchone.

H. W.

Structure of the triterpenes. C. W. PICARD, K. S. SHARPLES, and F. S. SPRING (Chem. and Ind., 1939, 58–59; cf. A., 1938, II, 416, 448).—On the assumption that the hydrocarbon obtained by dehydrogenating basseol is identical with that from hederagenin, i.e., 1 : 2 : 6-trimethylphenanthrene (cf. Ruzicka and Smith, A., 1939, II, 80), structures are suggested for basseol and for β -amyrenol. Any possibility, during cyclisation of basseol, of migration of an inert ethenoid linking is discounted by the fact that dihydrobasseol (bassenyl) acetate is oxidised to “ β -amyrenyl acetate oxide” (β -amyranonyl acetate), m.p. 293°, obtained also by oxidising β -amyrenyl acetate (formulae given). A modified formulation is recorded for oleanolic acid, which allows representation of keto-oleanolic acid as a γ -keto-acid, and of isoketo-oleanolic acid as a δ -keto- $\beta\gamma$ -unsaturated acid; the relative ease of saponification of the derived esters is thus more easily understood.

A. T. P.

Active principles of *Cannabis indica* resin. I. T. S. WORK, F. BERGEL, and A. R. TODD (Biochem. J., 1939, 33, 123–127).—The resin obtained from Indian hashish has b.p. 185–190°/0.6 mm. *p*- $NO_2 \cdot C_6H_4 \cdot COCl$ in C_5H_5N yields cannabinol *p*-nitrobenzoate (I), m.p. 160° (*p*-aminobenzoate, m.p. 149–150°), and a non-cryst. ester (II). Hydrolysis of (I) yields cannabinol as an oil which is very toxic in rabbits but gives a negative Gayer test (abolition of corneal reflex). The hydrolysis product of (II), after adsorption on Al_2O_3 , yields a product which gives a positive Gayer test in a dose of 0.25 mg. per kg. of body-wt.

P. G. M.

Beech lignin. O. MÜLLER and K. STORCH (Ber., 1939, 72, [B], 73–76).—Red beech is extracted with 4% NaOH at room temp., whereby a portion of the lignin (I) is dissolved. Treatment of the alkaline solution with Me_2SO_4 gives an ochre-yellow product identical in properties and analytical composition

with methyl-lignin. Acidification of the alkaline solution, after removal of hemicelluloses by $\text{MeOH} \cdot \text{H}_2\text{SO}_4$, ppts. (I) closely allied to cuproxam lignin; it condenses with $p\text{-C}_6\text{H}_4\text{Cl} \cdot \text{OH}$. Evidence is thus afforded that (I) is an actual substance formed under natural conditions. H. W.

Constituents of resins. XI. Resin alcohols of lactucarium. K. H. BAUER and K. BRUNNER (Arch. Pharm., 1938, 276, 605–617).—Extraction of lactucarium with 96% EtOH gives α - (I), m.p. 239–240°, and β -lactucerin (II), m.p. 231–233°. The mixture obtained by alkaline hydrolysis of the light petroleum extract is separated into α - (III), m.p. 223–224°, $[\alpha]_D^{25} + 89.33^\circ$ in CHCl_3 [acetate = (I); benzoate, m.p. 255–257°], and β -lactucrol (IV), $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. 178–180°, $[\alpha]_D^{25} + 50.77^\circ$ in CHCl_3 [acetate = (II); benzoate, m.p. 222–224°; p -bromobenzoate, m.p. 208–210°] (cf. A., 1929, 1187), which are saturated towards Br and KMnO_4 , but give a colour with $\text{C}(\text{NO}_2)_4$. CrO_3 -oxidation yields α -, m.p. 178–180° (oxime, m.p. 253–255°; 2:4-dinitrophenylhydrazone, m.p. 263–265°), and β -lactucrone, m.p. 186–188° (oxime, m.p. 235–236°; 2:4-dinitrophenylhydrazone, m.p. 243–244°), but a crude (III) yielded also γ -lactucrone, m.p. 153–155° [oxime, m.p. 239–240°; 2:4-dinitrophenylhydrazone, m.p. 255–257° (decomp.)]. More profound CrO_3 -oxidation of (III) gives also an acid, $\text{C}_{21}\text{H}_{34}\text{O}_3$, m.p. 204–205°, but (IV) yields similarly an acid, $\text{C}_{20}\text{H}_{32}(\text{CO}_2\text{H})_2$, loses gas at $\sim 115^\circ$, m.p. 158–160°. With H_2O_2 -AcOH at 100° (III) gives α -lactucrol oxide, m.p. 152–154° (acetate, m.p. 208–210°), but (IV) gives an unsaturated diacetate, $\text{C}_{34}\text{H}_{54}\text{O}_4$, m.p. 245–246°. H_2 - PdSO_4 converts (IV) with difficulty into dihydro- β -lactucrol, m.p. 191–193° (acetate, m.p. 250–251°). With PCl_5 in light petroleum (III) or (IV) gives lactucadiene (previously termed lactucene), $\text{C}_{30}\text{H}_{48}$, m.p. 153–154°; the compound previously termed lactucane is renamed lactucene. (II) is related to (IV) as $\text{CH}_2\text{R} \cdot \text{CHR}' \cdot \text{OH}$ is to $\text{OH} \cdot \text{CHR} \cdot \text{CH}_2\text{R}'$. R. S. C.

Constituents of natural phenolic resins. XIV. Synthesis of dl-, d-, and l-matairesinol dimethyl ether. R. D. HAWORTH and D. WOODCOCK (J.C.S., 1939, 154–156).—Veratraldehyde, $(\text{CH}_2\text{CO}_2\text{Na})_2$, and NaOEt give meso- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic acid, m.p. 223–224°, which with Ac_2O affords dl-(trans)- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic anhydride, m.p. 110–112°, reduced (Al-Hg) to dl-(trans)- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)butyrolactone (I), m.p. 113–115° [Br_2 , m.p. 112–113°, and $(\text{NO}_2)_2$ -derivatives, m.p. 191–192°], and hydrolysed to dl- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic acid (+4 H_2O), m.p. 95–105°. Resolution of this acid, through the strychnine salts [strychnine salt of l-acid (+3 H_2O), decomp. about 240° , $[\alpha]_D^{25} - 27.3^\circ$ in CHCl_3], gives d- (+3 H_2O), $[\alpha]_D^{25} + 25.8^\circ$ in CHCl_3 , and l- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic acids (+3 H_2O), m.p. 95–105°, $[\alpha]_D^{25} - 25.3^\circ$ in CHCl_3 . From these acids, the corresponding active anhydrides and lactones can be obtained: d(-), m.p. 131°, $[\alpha]_D^{25} - 37.6^\circ$ in COMe_2 , and l(+)- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)succinic anhydrides, m.p. 131°, $[\alpha]_D^{25} + 38.4^\circ$ in COMe_2 ; l-(trans)- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)butyrolactone, m.p. 127°, $[\alpha]_D^{25} - 32.3^\circ$ in CHCl_3 [Br_2 -deriv-

ative, m.p. 123° , $[\alpha]_D^{25} - 39.8^\circ$ in CHCl_3 ; $(\text{NO}_2)_2$ -derivative, m.p. 172 – 173° , $[\alpha]_D^{25} - 124^\circ$ in CHCl_3], and d-(trans)- $\alpha\beta$ -di-(3:4-dimethoxybenzyl)butyrolactone, m.p. 126° , $[\alpha]_D^{25} + 32.2^\circ$ in CHCl_3 [Br_2 -derivative, m.p. 123° , $[\alpha]_D^{25} + 40.2^\circ$ in CHCl_3 ; $(\text{NO}_2)_2$ -derivative, m.p. 173 – 174° , $[\alpha]_D^{25} - 126^\circ$ in CHCl_3]. (I) and its d- and l-forms are identical with natural dl-, d-, and l-matairesinol Me_2 ether, respectively. F. R. S.

Acids of the juice of Euphorbia biglandulosa. Desf. I. N. P. KIRJALOV (J. Gen. Chem. Russ., 1938, 8, 740–745).—The dried juice contains 15% of Ca salt of biglandulic acid, $\text{C}_7\text{H}_8\text{O}_2(\text{CO}_2\text{H})_2 \cdot \text{H}_2\text{O}$, m.p. 170 – 171° (anhydride, m.p. 210 – 212° ; Me_2 ester, m.p. 63 – 64° ; Et_2 ester, m.p. 57 – 58°), converted by heating with red P and HI into dihydrobiglandulolactone, m.p. 129 – 131° , and by hydrogenation (Pd catalyst) into dihydrobiglandulic acid, m.p. 165° (Me_2 ester, m.p. 56°). R. T.

Catalytic hydrogenation of the furan ring by the continuous method. N. I. SCHUIKIN and V. I. BUNINA (J. Gen. Chem. Russ., 1938, 8, 669–673).—27:73 Ni-Al alloy treated with 10% NaOH yields a very active and stable catalyst for hydrogenating furan or sylvan to the H_4 -derivatives, at 100 – 140° . R. T.

Synthesis of γ -oxides by catalytic hydrogenation of the furan ring. N. I. SCHUIKIN, E. V. SCHEMASTINA, and E. D. TSCHERKASOVA (J. Gen. Chem. Russ., 1938, 8, 674–679).—The hydrazone of 2-acetyl-5-methylfuran heated with KOH (Pt catalyst) yields 2-methyl-5-ethylfuran, b.p. 116 – $118^\circ/742$ mm.; this is hydrogenated (Pd-asbestos catalyst, activated with KOH) at 150° to 2-methyl-5-ethyltetrahydrofuran, b.p. 118 – $119^\circ/756$ mm. 2-n-Propylfuran similarly yields 2-n-propyltetrahydrofuran. R. T.

Tetrahydrofurfuryl mesityl oxide oxalate.—See B., 1939, 222.

Constitution of karanjin from the roots of Pongamia glabra. Vent. B. L. MANJUNATH, A. SEETHARAMIAH, and S. SIDDAPPA (Ber., 1939, 72, [B], 93–96).—Karanjin (I), m.p. 158.5° , becomes intensely yellow when exposed to sunlight or ultraviolet light. It is demethylated (HI, d 1.7, and boiling Ac_2O) to the corresponding OH-compound, m.p. 199 – 200° (acetate, m.p. 177°). Degradation of (I) with boiling KOH-EtOH affords 3-hydroxybenzofuran-4-carboxylic acid (II), m.p. 218° (decomp.), BzOH, and 3-hydroxy-4-methoxyacetylbenzofuran (III), m.p. 96° (3-methoxy-4-methoxyacetylbenzofuran, m.p. 87°). With H_2O_2 (II) in alkaline solution gives furan-2:3-dicarboxylic acid. (II) is decarboxylated by Cu-bronze in quinoline at 180 – 200° to 4-hydroxycoumarone and transformed by O_3 in CHCl_3 into 2:4-dihydroxy-3-formylbenzoic acid. (I) is obtained synthetically from (III), Bz_2O , and NaOBz at 180 – 185° . H. W.

Chalkones: new synthesis of chrysin, apigenin, and luteolin. W. A. HUTCHINS and T. S. WHEELER (J.C.S., 1939, 91–94).—o-Hydroxychalkone dibromides in general give flavones when they are heated above the m.p. or are treated with KCN-EtOH. Bromination of 2-hydroxy-4:6-dimethoxyphenyl styryl ketone affords 5-bromo-2-hydroxy-4:6-

dimethoxyphenyl α -*di*-bromo- β -*phenylethyl* ketone, m.p. 186°, which, when heated above the m.p. under reduced pressure, gives 6-bromo-5:7-dimethoxyflavone, m.p. 242°, converted by HI into chrysin. Apigenin is similarly derived from 5-bromo-2-hydroxy-4:6-dimethoxyphenyl α -*di*-bromo- β -*p*-anisylethyl ketone, m.p. 165°, and 6-bromo-5:7:4'-trimethoxyflavone, m.p. 250°. The latter compound with NaOH yields 4-bromo-3:5-dimethoxy-1-anisylidenecoumaran-2-one, m.p. 243°, and with C_5H_5N affords 5-bromo-2-hydroxy-4:6-dimethoxyphenyl *p*-methoxystyryl ketone, m.p. 184—185°. 5-Bromo-2-hydroxy-4:6-dimethoxyphenyl α -*di*-bromo- β -3:4-dimethoxyphenylethyl ketone, m.p. 165°, converted into 6-bromo-5:7:3':4'-tetramethoxyflavone, m.p. 258°, gives luteolin. F. R. S.

Chalkones: reactivity of aryl *o*-alkoxystyryl ketone dibromides and the synthesis of flavones therefrom. N. A. BHAGWAT and T. S. WHEELER (J.C.S., 1939, 94—96).—Aryl β -2-dialkoxystyryl ketones yield flavones when treated with HBr—AcOH; in both the *o*- and the *p*-alkoxystyryl dibromides, the side-chain halogen adjacent to the nucleus containing the alkoxy-group is replaced by alkoxy when treated with alcohols. The following are described: *Ph* 5-bromo-2-methoxystyryl ketone (+2H₂O), m.p. 110°; *Ph* α -*di*-bromo- β -5-bromo-*o*-anisyl ketone, m.p. 158°; *Ph* α -*di*-bromo- β -*m*-anisylethyl ketone, m.p. 122°; *p*-tolyl α -*di*-bromo- β -5-bromo-*o*-anisylethyl ketone, m.p. 159—160°; *Ph* α -bromo-*o*-methoxystyryl ketone, m.p. 106°; *Ph*, m.p. 103—104°, and *p*-tolyl α -5-*di*-bromo-*o*-methoxystyryl ketone, m.p. 127°; *Ph* α -bromo-*m*-methoxystyryl ketone, m.p. 100—101°; *Ph* 5-bromo- β -2-dimethoxystyryl ketone, m.p. 122°, and the *p*-tolyl compound, m.p. 96°; *Ph*, m.p. 127°, and *p*-tolyl 5-bromo-2-methoxy- β -ethoxystyryl ketone, m.p. 113°; *Ph* 6-bromo- β -3-dimethoxy-, m.p. 93°, and -3-methoxy- β -ethoxy-styryl ketone, m.p. 96°; benzoyl-5-bromo-*o*-anisylmethane, m.p. 96°, and the bromobenzoyl compound, m.p. 166°; 5-bromo-*o*-anisoyl-*p*-toluylmethane, m.p. 122°, and the *Br*-compound, m.p. 178°; and 6-bromo-4'-methylflavone, m.p. 197°. F. R. S.

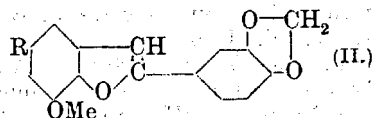
Chalkones: reactivity of naphthyl *p*-alkoxystyryl ketones and their dihalides. G. V. DESHMUKH and T. S. WHEELER (J.C.S., 1939, 96—98).—The following chalkones are described: 1-hydroxy-2-naphthyl 6-bromo-3:4-methylenedioxy-styryl ketone, m.p. 210°, and its 1-Ac, m.p. 173—174°, and 1-OMe-derivatives, m.p. 144—145°. Chalkones condense with $OAc \cdot CH_2 \cdot CO_2Et$ to form *Et* 4-phenyl-6-(6'-bromo-3':4'-methylenedioxyphenyl)- Δ^3 -cyclohexen-2-one-1-carboxylate, m.p. 133—134°, and *Et* 4-(1'-hydroxy-2'-naphthyl)-6-(6''-bromo-3'':4''-methylenedioxyphenyl)- Δ^3 -cyclohexen-2-one-1-carboxylate, m.p. 219—220°. Halogenation of the chalkones leads to 4-bromo-1-hydroxy-2-naphthyl 6-bromo-3:4-methylenedioxy-styryl, m.p. 249°, and α -*di*-bromo- β -(6-bromo-3:4-methylenedioxyphenyl)ethyl ketone, m.p. 215—216° (1-OMe-derivative, m.p. 187—188°); 1-acetoxy-2-naphthyl α -*di*-bromo- β -(6-bromo-3:4-methylenedioxyphenyl)ethyl ketone, m.p. 184°; and *Ph* α -*di*-chloro- β -(6-bromo-3:4-methylenedioxyphenyl)ethyl ketone, m.p. 149—150°. With $NH_3 \cdot EtOH$ these dihalides give *Ph* 6-bromo- β -amino-3:4-methylenedioxy-styryl ketone, m.p. 153°, and β -benzoyl- α -(6-bromo-3:4-methylenedioxyphenyl)propio-

nitrile, m.p. 120°. Interaction with alcohols affords 4-bromo-1-methoxy-2-naphthyl α -bromo- β -ethoxy- β -(6-bromo-3:4-methylenedioxyphenyl)ethyl ketone, m.p. 126—127°, and the corresponding β -OMe-compound, m.p. 150—151°. C_5H_5N with the chalkones gives 4-bromo-1-methoxy-2-naphthyl α :6-*di*-bromo-3:4-methylenedioxy-styryl ketone, m.p. 127—128°, and *Ph* α :6-*di*-bromo-, m.p. 123—124°, and α -chloro-6-bromo-3:4-methylenedioxy-styryl ketone, m.p. 125°, whilst $NHPh \cdot NH_2$ yields 1:3-diphenyl-5-(6'-bromo-3':4'-methylenedioxyphenyl)pyrazole, m.p. 163—164°. Chalkone dihalides not containing OH *o*- to the CO-group give β -alkoxystyryl derivatives on treatment with excess of NaOEt—EtOH, whilst those containing OH *o*- to CO yield flavones unless a β -alkoxy-compound is immediately formed: *Ph* 6-bromo- β -ethoxy-, m.p. 134—135°, and - β -methoxy-3:4-methylenedioxy-styryl ketone, m.p. 79—80°; 6-bromo-3:4-methylenedioxydibenzoylmethane, m.p. 125—126°; 6:6'-*di*-bromo-, m.p. above 275°, and 6'-bromo-3:4'-methylenedioxy-7:8-benzoflavone, m.p. 245—246°; and 6'-bromo-3':4'-methylenedioxy-1-benzylidene-5:6-benzocoumaran-2-one, m.p. 264°. F. R. S.

Colorimetric determination of α -tocopherol (vitamin-E). A. EMMERIE and C. ENGEL (Rec. trav. chim., 1938, 57, 1351—1355; cf. Karrer *et al.*, A., 1938, II, 466).— α -Tocopherol and $FeCl_3$ in EtOH (with or without C_6H_6) give a Fe^{II} salt which is determined colorimetrically with 2:2'-dipyridyl (better than *o*-phenanthroline); the results are comparable with those obtained by the potentiometric titration with $AuCl_3$. Carotene is completely oxidised and decolorised by $FeCl_3$ in presence of dipyridyl.

A. T. P.

Egonol. Synthesis of two egonol degradation products—dihydroconiferyl alcohol and styraxinolic aldehyde. S. KAWAI and N. SUGIYAMA (Proc. Imp. Acad. Tokyo, 1938, 14, 348—352; cf. A., 1938, II, 501; 1939, II, 29, 80).—The substance (I) obtained by vac. distillation of styraxinolic acid (*bis*-*p*-nitrobenzoate) differs from both 2-methoxy-4-methyl-6- and 2-methoxy-6-methyl-4- β -hydroxyethylphenol, which have been synthesised. (I) is oxidised ($KMnO_4$) to veratric acid, and is identical with 2-methoxy-4- ω -hydroxy-*n*-propylphenol (dihydroconiferyl alcohol) (*bis*-benzoate, -*p*-nitrobenzoate, and -phenylcarbamate), which has been synthesised (cf. Nomura *et al.*, A., 1928, 1005), and converted (Reimer-Tiemann) into styraxinolic



aldehyde (identical with that obtained from egonol). Egonol is therefore (II) with $R = [CH_2]_3 \cdot OH$. No details or analyses are given. An explanation of the colours given by egonol and by 2-phenylcoumarone with conc. H_2SO_4 is suggested.

A. LI.

Natural coumarins. XL. Coumarins from the drug, Semen angelicæ. E. SPÄTH and F. VIERHAPPER (Monatsh., 1938, 72, 179—189).—Isolation of imperatorin (I) (0.5%), bergapten (0.1%), umbelliprenin (0.04%), a phenol (0.03%), m.p. 224—

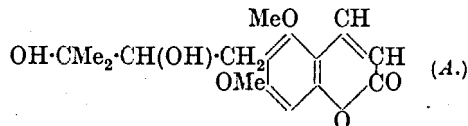
226°, xanthotoxin (0.02%), and xanthotoxol (0.02%) from the seeds of *Angelica archangelica*, L., is described (cf. A., 1937, II, 163, and following abstract). Removal of (I) is best effected by converting it by distillation into the phenolic *alloimperatorin*.

R. S. C.

Natural coumarins. XLIII. Synthesis of *isoimperatorin* and of *oxypeucedanin*. E. SPÄTH and E. DOBROVOLNY (Ber., 1939, 72, [B], 52—53).—Bergaptol (I) is converted by prenyl [γ -methyl- Δ^8 -butenyl] bromide and NaOMe-MeOH at 20° into *isoimperatorin* (II), thus effecting the complete synthesis of the latter compound since that of (I) has been effected by Späth *et al.* (A., 1937, II, 206). Since (II) has been transformed by BzO₂H into *oxypeucedanin* (III) (Späth and Kahovec), the synthesis of (III) is also accomplished.

H. W.

Natural coumarins. XLIV. Structural formula of toddalolactone. E. SPÄTH, B. B. DEY, and E. TYRAY (Ber., 1939, 72, [B], 53—56).—1:2:4:6-C₆H₂Me(OH)₃, conveniently obtained from 1:2:4:6-C₆H₂Me(NO₂)₃, is condensed with malic acid and conc. H₂SO₄ at 115° to a mixture of coumarins, converted by repeated treatment with CH₂N₂ into 5:7-dimethoxy-8- (I), m.p. 188—190°, and 5:7-dimethoxy-6-methylcoumarin (II), m.p. 132—133°. (II) is converted by NaOH and Et₂SO₄ followed by hydrolysis into 2:4-dimethoxy-6-ethoxy-3-methylcinnamic acid, oxidised (KMnO₄-NaOH) and then esterified (CH₂N₂) to Me₂ 2:4-dimethoxy-6-ethoxybenzene-1:3-dicarboxylate, m.p. 89—90°, identical with



the substance obtained by the degradation of toddalolactone (A., 1938, II, 451), which is therefore A; analogous treatment of (I) leads to Me₂ 4:6-dimethoxy-2-ethoxybenzene-1:3-dicarboxylate, m.p. 125—126°.

H. W.

[Pechmann reaction with ethyl α -acetylglutarate.] N. M. SHAH and R. C. SHAH (Ber., 1939, 72, [B], 215; cf. A., 1938, II, 502).—7:8-Dihydroxy-4-methylcoumarin-3-propionic acid has m.p. 185°.

H. W.

Preparation of flavones from *o*-aroyloxyacetophenones. V. V. ULLAL and T. S. WHEELER (Current Sci., 1938, 7, 280—281; cf. A., 1938, II, 452).—*o*-Aroyloxyacetophenones are more readily converted by NaOEt-EtOH than by Na-Et₂O or by Na-PhMe into ω -aroyl-*o*-hydroxyacetophenones.

J. L. D.

***iso*Flavans. I. Catalytic hydrogenation of *isoflavones*.** F. WESSELY and F. PRILLINGER (Monats., 1938, 72, 197—199).—Hydrogenation (Pd-C) of formononetin (A., 1933, 614) in AcOH gives 7-hydroxy-4'-methoxyisoflavan, m.p. 160° (sinters at 155.5°) (Me ether, m.p. 116.5—117.5°). *iso*Anthocyanidin could not be obtained from p-OMe-C₆H₄-CH₂-CHO and 2:4:1-OH-C₆H₃(OMe)-CHO.

R. S. C.

Dihydrothiophen. J. M. SLOBODIN (J. Gen. Chem. Russ., 1938, 8, 714—718).—(CH₂Br·CH)₂ and Na₂S in 90—95% EtOH yield a rubber-like product, (C₄H₆S₂)_n, a highly unstable liquid product (I), probably [S(CH·CH)₂]₂, and divinyl; in 50% EtOH at the b.p. the sole products are (I) and *dihydrothiophen*, b.p. 103—105° (compound with HgCl₂, m.p. 92—94°; methiodide, m.p. 122—123°).

R. T.

Thioindigo dyes with ability to couple, obtained from β -naphtholthioglycollic acids. E. JUSA and R. STECKLER (Monats., 1938, 72, 143—167).—Attempts to cyclise β -naphtholthioglycollic acids are described, the following being the most successful. Distillation of 2:7-OH·C₁₀H₆·S·CH₂·CO₂H, first at 180—220°/12 mm. and then at 10⁻³ mm., gives 4:7'-*dihydroxynaphtha*-2':1'-2:3-*thiophen* (I), m.p. 92°. 2:6-OH·C₁₀H₆·S·CH₂·CO₂H and P₂O₅ in hot C₆H₆ give 4:6'-*dihydroxynaphtha*-2':1'-2:3-*thiophen*, m.p. 130—133°, as 2-naphthol-6-thioglycolate; 4:6'-*dihydroxynaphtha*-1':2'-, m.p. 102—105°, 4:6'-*dihydroxynaphtha*-2':1'-, m.p. 130—133° (decomp.), 4:7'-*dihydroxynaphtha*-1':2'-, m.p. 137—139° (decomp.), -2:3-*thiophen*, and (I) are similarly obtained. The products are oxidised by air to *dyes*, which have little val. owing to the care necessary for prep. (Na₂S₂O₄) of vats and to the dull tone and lack of substantivity or fastness to light of the products obtained therefrom by coupling.

R. S. C.

Stereoisomeric forms of 2-piperidino- and 2-dimethylamino-methylcyclopentanol. C. MANNICH and P. SCHALLER (Arch. Pharm., 1938, 276, 575—582).—Piperidine hydrochloride, 40% aq. CH₂O, and cyclopentanone at 100° give 2-piperidinomethylcyclopentanone, b.p. 123—125°/16 mm. [semicarbazone, m.p. 195°; oxime, m.p. 132—133°; phenylhydrazone, m.p. 88—89° (hydrochloride, m.p. 161—162°)], the hydrochloride, m.p. 145° (decomp.), of which at ~160° gives 2-methylenecyclopentanone, an oil [semicarbazone, m.p. 219—220° (decomp.)], and with Na-Hg gives α - (I), b.p. 130—132°/11 mm. (hydrochloride, m.p. 210—211°; benzoate, m.p. 182—183°), and β -, b.p. 133—135°/14 mm. (hydrochloride, m.p. 204°; benzoate, m.p. 135—137°), forms of 2-piperidinomethylcyclopentanol, separated by way of the p-nitrobenzoates, m.p. 226—227° (decomp.) and 187—188°, respectively. SOCl₂-CHCl₃ converts (I) into 1-chloro-2-piperidinomethylcyclopentane hydrochloride, m.p. 186—187°. Similarly are prepared 2-dimethylaminomethyl-cyclopentanone, b.p. 88—90°/15 mm. [hydrochloride, m.p. 131—132°; semicarbazone, m.p. 184—185° (decomp.); oxime, m.p. 158—159°], and cyclopentanol, α -, b.p. 95—97°/12 mm. [hydrochloride, m.p. 144—145°; benzoate, m.p. 199—200°; p-nitrobenzoate, m.p. 220° (decomp.)], and β -form, b.p. 96—98°/14 mm. (hydrochloride, m.p. 134—136°; benzoate, m.p. 177°; p-nitrobenzoate, m.p. 178—179°), and 1-chloro-2-dimethylaminocyclopentane, b.p. 80—82°/14 mm. [hydrochloride, m.p. 176—177°; methiodide, m.p. 164—165° (decomp.); methochloride, m.p. 144—146°].

R. S. C.

Enimine betaines. I. F. KRÖHNKE (Ber., 1939, 72, [B], 83—89).—Addition of Br to CH₂Bz·CN in

CHCl_3 followed successively by $\text{C}_5\text{H}_5\text{N}$ and BzOH gives the *enol* form of ω -cyanophenacylpyridinium benzoate (I), $\text{OH}\cdot\text{CPh}\cdot\text{C}(\text{CN})\cdot\text{NC}_5\text{H}_5\cdot\text{OBz}$, m.p. 149—150°, converted by N-NaOH into the free *enol*-betaine, m.p. 142—143° (*picrate*, m.p. 173° after softening). $\text{CH}_2\text{Br}\cdot\text{CN}$ and $\text{C}_5\text{H}_5\text{N}$ in C_6H_6 at room temp. gradually yield cyanomethylpyridinium bromide (II), m.p. 161° (corresponding *perchlorate*, m.p. 125°), converted by BzCl and N-NaOH in CHCl_3 into (I). ω -Cyanomethylpyridinium *picrate* has m.p. 142—143°. (II) and $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ in EtOH containing NHET_2 yield the green *nitrone*, $\text{CN}\cdot\text{CH}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, m.p. >140° (decomp.) dependent on the rate of heating. Cyanomethylisoquinolinium bromide has m.p. 196—197°. $\text{CHPhBr}\cdot\text{CN}$ affords cyanobenzylpyridinium bromide, m.p. 160° (corresponding *perchlorate*, m.p. 121°), whence the corresponding betaine. Cyanobenzylisoquinolinium bromide, m.p. 176° (decomp.), gives a violet ppt. with $\text{N-K}_2\text{CO}_3$. Similarly a green ppt. is obtained from cyanobenzylquinolinium *perchlorate*, m.p. 159°. $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ affords cyanocarbethoxymethylpyridinium betaine, m.p. 112—113° (*picrate*, 123—124°); Et_3 tricyanotrimethylenetricarboxylate, m.p. 119—120°, is obtained as by-product.

H. W.

3-Diazo-2-phenylindole. IV. S. CAPUANO (Gazzetta, 1938, 68, 733—737).—The reaction between 3-amino-2-phenylindole and $\text{NaNO}_2\text{-AcOH}$ (A., 1938, II, 68), when interrupted before completion, gives a substance, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_4$, decomp. 172°, which in AcOH forms diazophenylindole.

E. W. W.

Quinoline derivatives as sources of medicinal products. VII. Anti-malarial compounds with branched side-chains in position 8, also 6-chloro- and 6-hydroxy-derivatives, and the influence of dimethylamino- and amino-groups in the side-chain. O. J. MAGIDSON and M. D. BOBISCHEV (J. Gen. Chem. Russ., 1938, 8, 899—915).— $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{COMe}$ and Na-Hg in dil. AcOH yield $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{OH}$, b.p. 109—110°/52 mm., which with SO_2Cl_2 in C_6H_6 gives $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{CHMeCl}$ (I), and with HBr gives β -bromo-8-diethylaminobutane, b.p. 89—95°/9 mm. This condensed with 8-amino-6-methoxyquinoline (II) in EtOH (12 hr. at 105°, then 8 hr. at 110°) gives 8-(γ -diethylamino- α -methylpropyl)amino-6-methoxyquinoline (III), b.p. 203—206°/4 mm. [*dimeconate*, m.p. 145° (decomp.)]; the yield of (III) obtained with (I) is somewhat smaller. NHET_2 and propylene oxide in EtOH at the b.p. yield $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NET}_2$, which with SO_2Cl_2 in Et_2O affords β -chloro- α -diethylaminopropane, b.p. 73—75°/50 mm. This with (II) in EtOH (36 hr. at 120°) yields 8-(β -diethylamino- α -methyl-ethyl)amino-6-methoxyquinoline (IV), b.p. 185—190°/3 mm. The product of condensation of $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ and $\text{Cl}\cdot[\text{CH}_2]_3\cdot\text{NET}_2$ (V) in xylene (15 hr. at 130°) is hydrolysed with 35% H_2SO_4 to α -diethylaminohexan- ϵ -one, b.p. 95—101°/10 mm., reduced (H_2 , Pt) to α -diethylaminohexan- ϵ -ol, b.p. 110—112°/10 mm., which with HBr gives β -bromo- ζ -diethylaminohexane. This with (II) (40 hr. at 110°, then 20 hr. at 120°) gives 8-(ϵ -diethylamino- α -methylamyl)amino-6-methoxyquinoline (VI), b.p. 205—208°/1.5 mm. 6-Chloro-8-

aminoquinoline with (V) (40 hr. at 110°) affords 6-chloro-8-(γ -diethylaminopropyl)aminoquinoline (VII), b.p. 186—188°/5 mm.; the analogous product with (I) (40 hr. at 120°) is 6-chloro-8-(γ -diethylamino- α -methylpropyl)aminoquinoline (VIII), b.p. 192—194°/6 mm. (II) and $\text{Cl}\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$ (40 hr. at 125°) yield 8-(γ -dimethylaminopropyl)amino-6-methoxyquinoline (IX), b.p. 190—191°/4 mm. 8-(γ -Diethylaminopropyl)amino-6-methoxyquinoline (X) with HBr at 170—175° (3 hr.) gives 8-(γ -diethylaminopropyl)-amino-6-hydroxyquinoline (XI), b.p. 240—250°/5 mm. (*dihydrobromide*, $+1\text{H}_2\text{O}$, m.p. 135—137°). The chemotherapeutic indices ($100 \times \text{min. curative/max. tolerated dose}$) of a series of substituted aminoalkyl-aminoquinolines are: (IV) 2, (III) 25, 8-(γ -diethylamino- α -methylbutyl)amino-6-methoxyquinoline 40, (VI) 25, (VII) 2-5, (VIII) 6-6, 8-(γ -aminopropyl)-amino-6-methoxyquinoline 13-3, (IX) 16-5, (X) 26-6, and (XI) 18-5.

R. T.

Quinoline derivatives with a basic side-chain.

C. MANNICH and O. SCHILLING (Arch. Pharm., 1938, 276, 582—592).—3 : 4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ (I) and 65% HNO_3 at -5° give 60—65% of the 6- NO_2 -derivative, forms, m.p. 153° and 168° (cf. lit.). A 60% yield of 6-nitroveratrylideneacetone, m.p. 179—180°, is similarly obtained. Piperidine hydrochloride, $(\text{CH}_2\text{O})_3$, and (I) in hot, abs. EtOH give γ -keto- ϵ -piperidino- α -6-nitro-3 : 4-methylenedioxyphenyl- Δ^a -butene hydrochloride, forms, m.p. 178° and 148—149° (free base unstable), obtained much less well by nitration of $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot[\text{CH}_2]_4\cdot\text{C}_5\text{H}_{11}\text{N}$ and converted by $\text{SnCl}_2\text{-HCl}$ into 6 : 7-methylenedioxy-2- β -1'-piperidinoethylquinoline, m.p. 135°. γ -Keto- ϵ -di-methyl-, m.p. 205—206°, and -ethyl-amino- α -3 : 4-methylenedioxyphenyl- Δ^a -butene hydrochloride, m.p. 139° (free base, m.p. 97°), γ -keto- ϵ -piperidino-, m.p. 186°, - ϵ -dimethylamino-, m.p. 185°, and - ϵ -diethylamino- α -3 : 4-methylenedioxyphenyl- Δ^a -butene hydrochloride, m.p. 179° (free base, m.p. 79°), 6 : 7-methylenedioxy-2- β -di-methyl- (II), m.p. 107° (*dihydrochloride*), and -ethyl-aminoethylquinoline, m.p. 80°, 6 : 7-dimethoxy-2- β -1'-piperidino-, an oil [*dihydrochloride*, m.p. 197—199° (decomp.)], - β -dimethylamino- (III), an oil (*hydrochloride*, m.p. 176°), and - β -diethylaminoethylquinoline, an oil (*dihydrochloride*, m.p. 182°), are obtained similarly. MeI attaches to the NMe_2 of (II) giving the *methiodide*, m.p. 203°, converted by NaOH into NMe_3 and 6 : 7-methylenedioxy-2-vinylquinoline, m.p. 138—139°, which with $\text{H}_2\text{-Pd}$ in AcOH gives 6 : 7-methylenedioxy-2-ethylquinoline, m.p. 119°, and with KMnO_4 gives 6 : 7-methylenedioxyquinoline-2-carboxylic acid, m.p. 240°. (III) gives similarly a *methiodide*, m.p. ~215° (decomp.), and thence 6 : 7-dimethoxy-2-vinyl-, an oil [*hydrochloride*, m.p. ~225° (decomp.)], and -2-ethyl-quinoline (*hydrochloride*, m.p. 211°), and 6 : 7-dimethoxyquinoline-2-carboxylic acid, m.p. 216°.

R. S. C.

Synthesis of isoquinoline acids. F. T. TYSON (J. Amer. Chem. Soc., 1939, 61, 183—185).— $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ and $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ at 100° give ~90% yields of o- (I), b.p. 167—170°/6 mm., m- (II), b.p. 152—154°/4 mm., and p-bromobenzylideneaminoacetal (III), b.p. 160—165°/4 mm. With $\text{H}_2\text{SO}_4\text{-P}_2\text{O}_5$ at 160° (I) and (III) give 8- (6%) and

6-bromoisoquinoline (29%), oils, which with CuCN at 250° give 8- (53%), m.p. 133°, and 6-cyanoisoquinoline (25%), m.p. 152°, hydrolysed by HCl at 150° to isoquinoline-8-, m.p. 292—294° (decomp.), and -6-carboxylic acid, m.p. 355—360° (decomp.), respectively. 4- and 5-Bromoisoquinoline (Claus *et al.*, A., 1893, i, 366) give similarly 4-, m.p. 104°, and 5-cyanoisoquinoline, m.p. 139°, and isoquinoline-4-, m.p. 264—266°, and -5-carboxylic acid (IV) (Jeiteles, A., 1895, i, 393), m.p. 280—282°. (II) gives mixed bromo- and cyano-isoquinolines, hydrolysed to (I) and isoquinoline-7-carboxylic acid, m.p. 295—297°, which are separated by crystallising the Na salts from aq. dioxan. R. S. C.

Direct introduction of the amino-group into aromatic and heterocyclic nuclei. V. Action of metallic amides on phenyl- and benzo-quinolines. F. W. BERGSTROM (J. Org. Chem., 1938, 3, 424—433).—2-Phenylquinoline (I) is converted by the prolonged action of KNH₂ in liquid NH₃ followed by hydrolysis into a diphenyltetrahydrodiquinolyl, m.p. >280°. Less protracted action with alkali amides in liquid NH₃ gives additive compounds of unknown structure but of the type, C₉H₈NPh.NaNH₂; (I) is regenerated from them by the action of NH₄ salts. On keeping, secondary additive compounds are formed which do not react with NH₄ salts to give (I) but react with KNH₂ (NaNH₂) and KNO₃ (NaNO₃) or Hg to give 4-amino-2-phenylquinoline, m.p. 164.0—164.9°, thus: (I) + 2KNH₂ + KNO₃ = KOH + KNO₂ + NH₃ + C₉H₈NPh.NHK (II) or (I) + 3KNH₂ + xHg = K₂Hg_x + 2NH₃ + (II). The yields of (II) are excellent. There is no evidence for or against the assumption that these reactions are stepwise. By using the same methods, 2(?) -amino-6-phenyl-, m.p. 243—243.5°, -8-phenyl-, m.p. 156—159°, -7:8-benzo-, m.p. 104—105° [hydrochloride, m.p. >288°; picrate, m.p. 259—262° (decomp.)], and -5:6-benzo-, m.p. 235°, -quinoline are obtained. In these cases the prep. may also be accomplished with Ba(NH₂)₂, when H₂ is evolved. 2-*p*-Tolylquinoline has not been converted into an NH₂-derivative. KNH₂ also converts 6- and 8-phenylquinoline into tars. The two benzoquinolines react with KNH₂ to form NH₂-derivatives in fair yield (25—35%) with small amounts of H₂. H. W.

Structure and absorption [spectra] of diamino-derivatives of acridine dyes. P. RAMART, M. GRUMEZ, and M. MARTYNOFF (Compt. rend., 1938, 207, 1106—1109).—Hydrochlorides of acridine-yellow and -orange, benzoflavine, and tetramethyl-flavosine in H₂O or EtOH have similar absorption spectra (*p*-quinonoid form). The spectra of 0.0005N. solutions of the bases resemble those of the hydrochlorides, but in 0.0005N. solutions the spectra are different, due to the *o*-quinonoid form, which is the only one present in 0.1N-NaOH or anhyd. dioxan. J. L. D.

Hydroxy- and methoxy-derivatives of acridine. S. M. SCHERLIN, G. I. BRAZ, A. J. JAKUBOVITSCH, E. I. VOROBIEVA, and F. E. RABINOVITSCH (J. Gen. Chem. Russ., 1938, 8, 884—898).—1-Methoxy-acridone (I), NaHCO₃, and Na-Hg in EtOH (CO₂ atm.) yield 1-methoxy-5:10-dihydroacridine, oxid-

ised by K₂Cr₂O₇ to 1-methoxyacridine (II); reduction of (I) with Na in boiling C₆H₁₁-OH, and oxidation of the product, gives a mixture of (II) and 1-hydroxy-acridine. 4:2:1-OMe-C₆H₃Cl·CO₂K and NH₂Ph in *iso*-C₅H₁₁-OH with Cu-bronze at 130—140° for 90 min. yield 5-methoxydiphenylamine-2-carboxylic acid, which with PCl₅ and AlCl₃ in C₆H₆ at 30—40° gives 2-methoxyacridone. This is reduced as above to 2-methoxy-5:10-dihydroacridine, m.p. 131—132°, oxidised (HNO₂) to 2-methoxyacridine, m.p. 248—250° (decomp.). 4-Methoxydiphenylamine-2'-carboxylic acid is condensed (PCl₅ and AlCl₃ in C₆H₆, at room temp.) to 3-methoxyacridone (III), m.p. 291—292° [Borsche *et al.* (A., 1933, 1170) give m.p. 263—265°]; condensation in boiling C₆H₆ yields 3-hydroxyacridone (IV), +H₂O, m.p. 337—340° (decomp.); (III) and (IV) are reduced as above to the corresponding 5:10-H₂-derivatives, m.p. 140—141° and 181—185°, respectively, and these are oxidised to 3-methoxy-[hydrochloride, m.p. 237—239° (decomp.)], or 3-hydroxy-acridine, sinters at 278°, m.p. 282—284°. 3-Methoxydiphenylamine-2'-carboxylic acid in C₆H₆ and PCl₅ in presence of AlCl₃, at room temp., yield a mixture of 2- and 4-methoxyacridone, m.p. 155—156°. 2:5-Dimethoxyaniline in *iso*-C₅H₁₁-OH and *o*-C₆H₄Cl·CO₂K in presence of Cu and CuCl (3 hr. at 135—140°) yield 2:5-dimethoxydiphenylamine-2'-carboxylic acid, m.p. 164.2—164.8°, which with PCl₅ and AlCl₃ in C₆H₆ (2 hr. at the b.p.) gives 5-chloro-1:4-dimethoxyacridone (V), +EtOH, m.p. 200—201°, whilst with POCl₃ at 130—140° the product is 5-chloro-1:4-dimethoxyacridine, +2H₂O, m.p. 145.5—146°. This when boiled with HCl yields 1:4-dimethoxyacridone, m.p. 222—223°, also obtained from (V) and PCl₃ at 70°, and from which 1:4-dimethoxyacridine, m.p. 130—130.5°, is obtained as before. 2-Chloro-3-methoxybenzoic acid, *o*-anisidine, K₂CO₃, and Cu-bronze in boiling *iso*-C₅H₁₁-OH (3 hr.) yield 2:2'-dimethoxydiphenylamine-6-carboxylic acid, m.p. 176—177°, which with POCl₃ (2.5 hr. at 160°) gives 1:9-dimethoxyacridone, m.p. 274—275°, converted as above via the 5:10-H₂-derivative, m.p. 91—92.5°, into 1:9-dimethoxyacridine, m.p. 195—196°. R. T.

meso-Derivatives of acridine. IX. Chlorides of diphenylaminecarboxylic acids, and their conversion into acridones. N. S. DROZDOV (J. Gen. Chem. Russ., 1938, 8, 937—942).—The following acid chlorides are obtained from diphenylamine-carboxylic acids and PCl₅ in light petroleum (at room temp. or at the b.p.): chloride of 4'-methoxy-, m.p. 73°, 5-chloro-4'-methoxy-, m.p. 110—111°, and 2':4'-dinitro-diphenylamine- (I), and diphenylamine-2-carboxylic acid, m.p. 50°. (I) fused with PhOH at 100° yields Ph 2':4'-dinitrodiphenylamine-2-carboxylate, m.p. 183—184°; the remaining chlorides give acridone under these conditions, or when heated at above their m.p. R. T.

Synthesis of the next higher and lower homologues of *l*-carnosine: γ -aminobutyryl- and glycyl-*l*-histidine. M. HUNT, and V. DU VIGNEAUD (J. Biol. Chem., 1939, 127, 43—48).—Carbo-benzyloxyglycyl chloride (cf. A., 1932, 935) with histidine Me ester (I) in dry CHCl₃ at 0° affords a

product hydrolysed (NaOH at room temp.) to *carbobenzoyloxyglycyl-L-histidine* (II), m.p. 175°, $[\alpha]_D^{25} +22^\circ$ in H_2O , reduced (H_2 -Pd) in aq. HCl to *glycyl-L-histidine* (hydrochloride + $1H_2O$, m.p. 175°) (cf. A., 1931, 1191). Reduction (H_2 -Raney Ni) of aq. $CH_2Br \cdot CH_2 \cdot CO_2Na$ containing NaCN at 40–50° followed by interaction with $CH_3Ph \cdot COCl$ at 0° gives *carbobenzoyloxy- γ -aminobutyric acid* (III), m.p. 66°. (III) with PCl_5 in Et_2O at 0° affords the chloride, which with (I) in $CHCl_3$, followed by hydrolysis (cold 4N-NaOH) and reduction [as for (II)], affords *γ -aminobutyryl-L-histidine (sulphate)*, m.p. 235°, $[\alpha]_D^{25} +5^\circ$ in H_2O . Neither peptide in 20 times the dose of *L*-carnosine has any effect on the blood pressure of cats anaesthetised with amytal. The β - NH_2 -group in the acyl moiety of carnosine is mainly responsible for its depressor action. J. L. D.

Synthesis of barbituric acid derivatives with an acid side-chain. B. REICHERT and W. WILKE (Arch. Pharm., 1938, 276, 596–605).— $CRNa(CO_2Et)_2$ and $Br[CH_2]_3 \cdot CO_2Et$ in abs. EtOH give *Et_3 \Delta^5*-heptene- $\alpha\delta\delta$ -, b.p. 188–192°/12 mm., η -methyloctane- $\alpha\delta\delta$ -, b.p. 189–191°/11 mm., and ϵ -phenylpentane- $\alpha\delta\delta$ -tricarboxylate, b.p. 232–234°/15 mm. By condensation with $CO(NH_2)_2$ and NaOEt in EtOH at 150° are obtained γ -2:4:6-triketo-5-ethyl- (I), m.p. 222°, -5-n-propyl-, m.p. 208°, -5-isoamyl-, m.p. 191–192°, -5-allyl-, m.p. 182°, and -5-benzyl-, m.p. 214°, -hexahydro-5-pyrimidyl-n-butyric acid. Attempts to convert the *Et* ester, m.p. 112°, of (I) into the amide failed. Similar syntheses lead to *Et_3* diethylcarbamyldiethylmalonate, b.p. 194–196°/14 mm., $\beta\beta$ -dicarbethoxy-n-valer-, b.p. 198–200°/18 mm., Δ^5 -hexeno-, b.p. 192°/14 mm., and δ -phenylbutyrdiethylamide, b.p. 235–236°/8 mm., 2:4:6-triketo-5-ethyl-, m.p. 221°, -5-n-propyl-, m.p. 206–207°, -5-allyl-, m.p. 190°, and -5-benzyl-hexahydro-5-pyrimidylacetyl-diethylamide, m.p. 247–248°, 4:6-diketo-2-thio-5-n-propylhexahydro-5-pyrimidylacetyl-diethylamide (prep. at 170°), m.p. 196°, and 2:4:6-triketo-5-ethylhexahydro-5-pyrimidylbutyrdiethylamide, m.p. 172°. $Br[CH_2]_3 \cdot Cl$, $CHR(CO_2Et)_2$, and NaOEt in hot EtOH give $CH_2[CH_2 \cdot CR(CO_2Et)_2]_2$, which yield $\alpha\gamma$ -di-(2:4:6-triketo-5-ethyl-, m.p. 317–318°, -5-n-propyl-, m.p. 253–254°, and -5-allyl-hexahydro-5-pyrimidyl)propane, m.p. 218°, $\alpha\gamma$ -di-(2:4:6-triketo-1-methyl-5-ethyl-, m.p. 261°, and -5-benzyl-1-methyl-hexahydro-5-pyrimidyl)propane, m.p. 272–273°. *Et_4* $\alpha\eta$ -diphenylheptane- $\beta\beta\zeta\zeta$ -tetracarboxylate, m.p. 77°, b.p. 300–305°/12 mm., is described. R. S. C.

Substituted vinylbarbituric acids. I. iso-Propenyl derivatives. A. C. COPE and E. M. HANCOCK (J. Amer. Chem. Soc., 1939, 61, 96–98).— Et_2 alkylisopropenylmalonates with $CO(NH_2)_2$ or $CS(NH_2)_2$ and NaOEt in abs. EtOH at 105° give 5-methyl-, m.p. 181–181.5°, -ethyl-, m.p. 184–184.2°, -propyl-, forms, m.p. 149–150° and (unstable) 158–159.5°, respectively, -allyl-, m.p. 144.4–145°, -n-, m.p. 156–157°, and -iso-butyl-, m.p. 161.5–162.5°, -n-, m.p. 123–124°, and -iso-amyl-, m.p. 128–129°, -benzyl-, m.p. 231.5–232.5°, 1-methyl-5-ethyl-, m.p. 125.5–126°, 1:5-diethyl-, m.p. 67–68°, and 5-ethyl-1-allyl-, m.p. 65–66°, -5-isopropenylbarbituric acid and 5-methyl-, m.p. 154–155°, -ethyl-, m.p. 191–

192°, -propyl-, m.p. 184–185°, -allyl-, m.p. 176.5–177°, -n-, m.p. 160–161°, and -iso-butyl-, m.p. 164–165°, -n-, m.p. 139–140°, and -iso-amyl-, m.p. 165.5–166.5°, and -benzyl-, m.p. 157–158°, -5-isopropenylthiobarbituric acid. Pharmacological data are recorded. Alcoholysis during the preps. leads to smaller amounts of β -methyl- α -ethyl-, m.p. 151–151.5°, - α -n-, m.p. 115–116°, and - α -iso-butyl-, m.p. 128–128.2°, - α -n-, m.p. 111–112°, and - α -iso-amyl-, m.p. 108–109°, and - α -benzyl-, m.p. 122–122.5°, -crotonamide, the structure of which is shown by production of $COMe_2$, and not of CH_2O , by O_3 . *Et_2* benzylisopropenylmalonate boils at 141–142°/1 mm.

R. S. C.

Pyrimidines. CLX. Catalytic hydrogenation of 5- and 6-benzyluracils. J. C. AMBELANG and T. B. JOHNSON (J. Amer. Chem. Soc., 1939, 61, 74–77).—The CH_2Ph of 5- (I), but not of 6- (II), -benzyluracil is hydrogenated catalytically in EtOH. H_2 -Raney Ni at 175° reduces (II) to *benzylhydrouracil* (III), m.p. 223–224° (hydrolysed by 15% aq. NaOH to $CHPh \cdot CH \cdot CH_2 \cdot CO_2H$), but at 225° gives 2-keto-6-benzylhexahydropyrimidine (IV), m.p. 184–185°, obtained similarly from (III), oxidised to $BzOH$, and hydrolysed to $\alpha\gamma$ -diamino- δ -phenylbutane (dihydrochloride, m.p. 145–146°; Bz_2 derivative, m.p. 174–175°). H_2 -Cu- Cr_2O_3 at 200° converts (II) into (IV). H_2 -Raney Ni at 175° converts (I) in EtOH or, less well, dioxan into 5-benzylhydrouracil (V) (impure), m.p. 232°, but at 200–220° in EtOH gives slowly 2-keto-5-cyclohexylmethylhexahydropyrimidine, m.p. 221–223°. H_2 -Cu- Cr_2O_3 reduces (I) or (V) in EtOH (very slowly in dioxan) to 2-keto-5-benzylhexahydropyrimidine, m.p. 214–215°. R. S. C.

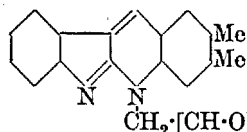
Pyrimidines and quinazolines.—See B., 1939, 177.

Simple cyanines. B. BEILSON and (Miss) F. M. HAMER (J.C.S., 1939, 143–151).—The known methods for preparing monomethincyanines are reviewed. 2-Thiolquinoline with Me_2SO_4 gives 2-methyl- (I), m.p. 55°, and with Et_2SO_4 affords 2-ethylthiolquinoline, b.p. 177–178°/26 mm. [ethiodide, m.p. 165° (decomp.); *etho*-p-toluenesulphonate, m.p. 116°]. (I) yields a methiodide, m.p. 193°, and metho-p-toluenesulphonate, m.p. 160°, and with EtI gives 2-ethylthiolquinoline methiodide, m.p. 185° (decomp.). This and 2-aminoquinoline ethiodide afford (K_2CO_3) 1-methyl-1'-ethyl-2:2'-azacyanine iodide [(1-methyl-2-quinoline)(1-ethyl-2-quinoline)azamethincyanine iodide], m.p. about 235° (decomp.); 1:1'-dimethyl-2:2'-azacyanine iodide, m.p. 273–275° (decomp.), is similarly prepared. 1-Methylthiolbenzthiazole forms a methiodide, m.p. 146° (decomp.), ethiodide (II), m.p. 135–137° (decomp.), and metho-p-toluenesulphonate, m.p. 167–168°. 1-Ethylthiolbenzthiazole yields an ethiodide, m.p. 95–96°. From the appropriate reagent and (II), the following dyes have been prepared: 2:2'-diethyl-5:6-benz-, m.p. 299° (decomp.), 2:2'-diethylsclena-, m.p. 284° (decomp.), 2:2'-diethyl-3:4-benzoxa-, m.p. 288° (decomp.), and 2:2'-diethyl-5:6-benzoxa-thiacyanine iodide, m.p. 278° (decomp.). Methylation of the appropriate reagent leads to 1-methylthiolbenzoxazole (III), b.p. 139–140°/21 mm., 2-methylthiol- β - (IV), m.p. 73° (from 2-thiol- β -naphth-

oxazole, m.p. 264°), and 1-methylthiol- α -naphthoxazole (V), m.p. 64°. Lepidine, (III), and Et *p*-toluenesulphonate give 2:1'-diethyloxa-4'-cyanine iodide, m.p. 233° (decomp.), and (V) with β -naphthaquinoline similarly forms 2:1'-diethyl-5:6:5':6'-dibenzoxa-2'-cyanine iodide, m.p. 288° (decomp.). MeI with (IV), (V), and (III) yields respectively 2-thio-1-methyl- (VI), m.p. 185–187°, and 1-thio-2-methyl-1:2-dihydro- α -naphthoxazole, m.p. 226°, and 1-thio-2-methyl-1:2-dihydrobenzoxazole, m.p. 133°; EtI and (V) give 1-thio-2-ethyl-1:2-dihydro- α -naphthoxazole, m.p. 215°. 1-Methylbenzthiazole, (VI), and Me *p*-toluenesulphonate afford 2:2'-dimethyl-3:4-benzoxathiacyanine *p*-toluenesulphonate, m.p. 262°. 2-Thio-1-methyl-1:2-dihydroquinoline and Me *p*-toluenesulphonate give a salt, m.p. 160–161°, which with 1-methylbenzthiazole methiodide forms 2:1'-dimethylthia-2'-cyanine iodide.

F. R. S.

Azines. W. BEDNARCZYK and L. MARCHLEWSKI (Biochem. Z., 1938, 300, 46–55).—Alloxan, $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, 2HCl and excess of NaOAc in H_2O at 100° give 2-hydroxy-3-carbamylcarbamylquinoxaline (I), m.p. 238–239°. 2-Hydroxy-3-*o*-aminophenylquinoxaline (II), m.p. 258–260°, is obtained by condensing acetylatisin with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ and hydrolysing the product. *N*-Ribitylaminoxyldine and isatin give *N*-ribityldimethylindophenazine (III). The absorption



(III.)

spectra of (I) in aq. and alkaline solution have been determined. In the former case the mol. extinction curve has 2 max. and 2 min., whilst in the latter case there are only 1 max. and 1 min. The absorption spectra of alcoholic solutions of indophenazine, (II), (III), and coumarophenazine together with their mol. extinction curves have been determined. J. N. A.

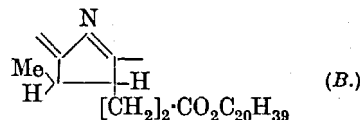
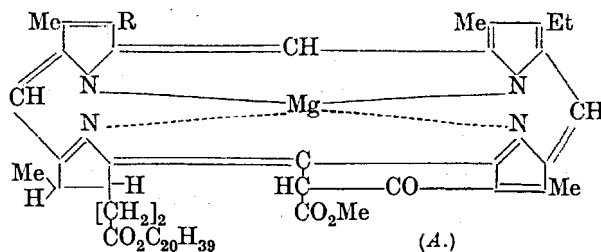
Union of nucleotides in ribonucleic acid. R. S. TIPSON and P. A. LEVENE (J. Biol. Chem., 1939, 127, 105–110).—The “guanine-uridylic acid” of Brederick and Richter (A., 1936, 868) is a mixture of ribonucleosides, nucleotides, and free purines.

J. L. D.

Constitution of polynucleotides. Deamination of yeast- and thymo-nucleic acid.—See A., 1939, III, 326.

Chlorophylls. LXXXIV. Chlorophyll. H. FISCHER and H. WENDEROTH (Annalen, 1939, 537, 170–177; cf. A., 1938, II, 297).—Oxidation of chlorophyll derivatives is so conducted that acidic and basic products are isolated or proved to be absent. Porphyrins, but not chlorins or phorbides, give hæmatic acid (I). Vinyl, HCO- , and $\text{CO}_2\text{H-}$ derivatives give no basic products, but deuterohæmin gives citraconimide (II), and pyrroporphyrin and phyllochlorin give a 1:2 mixture of (II) and methylethylmaleimide (III). Pyrrolines (crypto- and opso-pyrroline) give no (III), but crypto- and opso-pyrrole do so. Lævorotatory fractions are isolated from the acids obtained from phæopurpurin-7 [gives also (III)], phyllochlorin, mesophæophorbide-*a* [gives also (III)], and phæo-

phorbide-*b*, but not from pyrroporphyrin [gives also (I), (II), and (III)]. It follows that chlorophyll-*a* is (A) ($\text{R} = \text{CH}:\text{CH}_2$) or, less probably, a structure containing the unit (B) with the necessary rearrangement of the other linkings. Chlorophyll-*b* is (A) ($\text{R} = \text{CHO}$). Oxidation of bacteriochlorin- e_6 gives a dextro-rotatory basic and a lævorotatory acidic fraction; thus bacteriochlorophyll is probably a 3:4:7:8- H_4 -derivative, and bacteriochlorin and bacteriophorbide are derived from (B). The following oxidation products are also recorded, those not named being absent:



phæophorbide-*a*, pyrophæophorbide-*a*, chlorin- e_6 , and mesorhodochlorin give (II); phæoporphyrin- a_5 gives (I) and (II); deuterohæmin gives (I) and (II); protoporphyrin gives (I); rhodin- g_7 does not give (I), (II), or (III). R. S. C.

New case of chemoluminescence. II. Benzoporphyrins. V. J. H. HELBERGER and D. B. HEVÉR (Ber., 1939, 72, [B], 11–15; cf. A., 1938, II, 510).—Only a very slight luminescence, mainly at the zone of contact of solution and air, is observed when Mg phthalocyanine (I) is introduced into boiling, pure tetrahydronaphthalene (II), which thus behaves very differently from the technical product. The hypothesis that the active agent is a peroxide (III) of (II) is confirmed by the observation that this compound provokes luminescence slightly in boiling C_6H_6 , more markedly in boiling PhMe. Technical PhMe contains small amounts of a non-volatile, active material whilst pure PhMe can be “activated” by prolonged passage of air at 50–60°. Experiments in PhMe show that 1 mol. of (I) requires 13–16 mols. of (II) for complete reaction; the formation of H_2O and NH_3 is speedily obvious. The first phase of the change appears to result in the removal of Mg and the cyclic residue is then decomposed with formation of NH_3 and $\text{o-C}_6\text{H}_4(\text{CO})_2\text{NH}$. The necessary H_2O results from the decomp. of (III) into H_2O and 1-keto-1:2:3:4-tetrahydronaphthalene. Similar complexes of Zn and Pb behave analogously but more feebly. Cu and Fe complexes and metal-free pigments give luminescence with (III) only in solvents of high b.p. [PhCl; cymene (IV); tetrahydronaphthalene]. The luminescence of (I) is more marked in xylene than in PhMe and is particularly obvious in (IV). Zn tetrabenzoporphyrin and (I) give an unidentified substance, $\text{C}_{10}\text{H}_{16}\text{O}_2$, m.p. 157–158°. Peroxidised oil of turpentine and technical decahydronaphthalene are very “active,” whereas PhCl and PhBr are

ineffective. Little or no luminescence is observed when BuOH, amyl alcohol or acetate, dioxan, C_5H_5N , quinoline, piperidine, or Ac_2O is used.

H. W.

Phenylpropiolthio-*p*-chloroanilide. D. E. Worrall and E. Lavin (J. Amer. Chem. Soc., 1939, 61, 104—105).—*Phenylpropiolthio-*p*-chloroanilide* (I), m.p. 138—139° (decomp.), obtained from $CPh:CNa$ and $p-C_6H_4Cl-NCS$ in Et_2O at room temp., gives with NaOH in hot Et_2O a *dimeride*, m.p. 245—246° (decomp.), which with $Br-CHCl_3$ affords a poor yield of the *dibromide*, m.p. 229—230° (decomp.), of (I). With NH_2OH , (I) gives 3-*p*-chloroanilino-5-phenylisooxazole, m.p. 166—167° [and a small amount of 5-chloro-1-phenacylbenzthiazole, m.p. 192—193° (decomp.)], and thence 4-bromo-3-4'-chloro-2'-bromo-, m.p. 133—134°, 4-chloro-3-2':4'-dichloro-, m.p. 95—96°, and 4-nitro-3-4'-chloro-2'-nitro-anilino-5-phenylisooxazole, m.p. 165—166°. With N_2H_4 (I) yields 3-*p*-chloroanilino-5-phenylpyrazole, m.p. 174—175°, and thence 4-bromo-3-4'-chloro-2'-bromoanilino-5-phenylpyrazole, m.p. 198—199°. *Phenylpropiolthio-*m*-chloroanilide*, m.p. 115—116° (decomp.), also yields [as for (I)] a *polymeride*, m.p. 227—228° (decomp.).

R. S. C.

Reactions of phenylpropiol[thio]-*p*-iodoanilide and related thioamides. D. E. Worrall, M. Lerner, and J. Washnock, jun. (J. Amer. Chem. Soc., 1939, 61, 105—106).— $CPh:CNa$ and $RNCS$ in Et_2O give *phenylpropiol-*p*-iodoanilide*, m.p. 140—141° (*dimeride*, m.p. >173°), *m*-bromoanilide, m.p. 120—121° (*dimeride*, m.p. indefinite), *p*-phenetidine, m.p. 111—112° (*dimeride*, m.p. 199—200°), 4'-xenylamide, m.p. 128—129° (*dimeride*, m.p. 230—232°), and α -naphthalide, m.p. 184—185°, which with NH_2OH or N_2H_4 yield 3-*p*-iodoanilino-, m.p. 148—149°, and 3-4'-xenylamino-5-phenylisooxazole, m.p. 176—177°, 3-*p*-iodoanilino-, m.p. 175—176°, 3-*m*-bromoanilino-, m.p. 205—206°, and 3-4'-xenylamino-5-phenylpyrazole, m.p. 219—220°, converted by substitution into 4-bromo-, m.p. 172—173°, 4-chloro-, m.p. 151—152°, and 4-nitro-3-*p*-iodoanilino-5-phenylisooxazole, m.p. 243—244°, 4-bromo-3-2'-bromo-4'-iodoanilino-, m.p. 201—202°, 4-chloro-3-*p*-iodoanilino-, m.p. 206—207°, and 4-bromo-3-*m*-bromoanilino-5-phenylpyrazole, m.p. 178—179°. 4-Bromo-3-3'-bromo-, m.p. 130—131°, and 4-chloro-3-3':5'-dichloro-*p*-toluidino-5-phenylisooxazole, m.p. 229—230°, 3-*p*-toluidino-, m.p. 157—158°, 4-bromo-3-3'-bromo-*p*-toluidino-, m.p. 181—182°, and 4-nitro-3-3':5'-dinitro-*p*-toluidino-5-phenylpyrazole, m.p. 245—247°, are also prepared.

R. S. C.

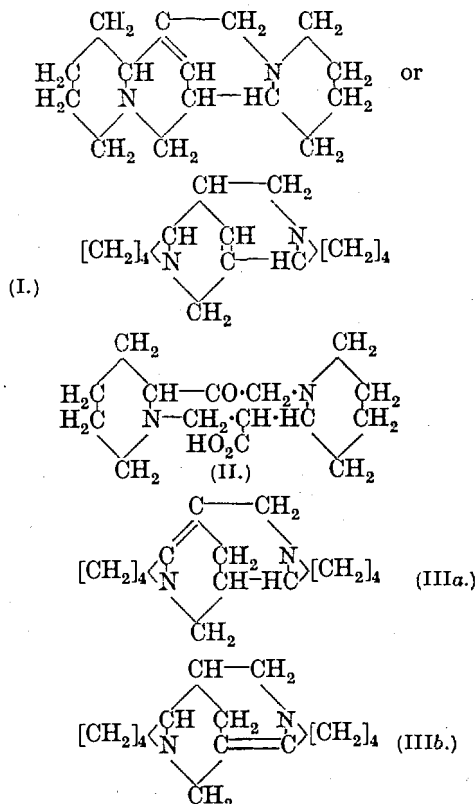
Cyanine dyes.—See B., 1939, 217, 218.

The green fluorescent pigment of *Pseudomonas fluorescens*. A. Turfreljer, J. P. Wibaut, and T. Y. Kingma Boltjes (Rec. trav. chim., 1938, 57, 1397—1404; cf. Turfitt, A., 1937, III, 145; Giral, A., 1937, III, 145).—The pigment (I) isolated by the Giral method (cf. György *et al.*, A., 1934, 461) (absorption on C; treating with $COMe_2-H_2O$; pptg. with phosphotungstic acid and decomp. with HCl) is isolated as an amorphous double salt, (?) $C_{32}H_{41}O_3N_7 \cdot 2HAuCl_4$. A second pigment in the culture (medium used: NH_4 lactate, K_2HPO_4 , and

$MgSO_4$ in H_2O , of p_H 7.2) is not absorbed on the C. (I) and H_2O_2-KOH afford salts, (?) $C_{27}H_{35}O_2N_7 \cdot 2HAuCl_4$, decomp. $\sim 170^\circ$, and (?) $C_{11}H_{16(18)}ON_8 \cdot 3AuCl$ or $C_{13}H_{25}O_2N_{13} \cdot 5AuCl$. (I) and soda-lime at 400° , in N_2 , give a compound, (?) $C_{32}H_{41}O_3N_7$, in which the green fluorescence persists. The configuration responsible, possibly of one O and a heterocyclic ring with 2 N, is stable.

A. T. P.

Lupin alkaloids. XVI. Oxidative degradation of Wolfenstein's dehydrosparteine. K. Winterfeld and M. Schirm (Arch. Pharm., 1938, 276, 544—552; cf. A., 1938, II, 72).—Wolfenstein's dehydrosparteine (I) (modified prep.; cf. A., 1927, 887), m.p. 172—173°, $[\alpha]_D^{25} -236^\circ$ in $CHCl_3$, -192° in $EtOH$ [aurichloride, $+H_2O$, m.p. 181° (decomp.); platinichloride, $+3.5H_2O$, m.p. 250° (decomp.); picrate, m.p. 181—182° (decomp.)], with $CrO_3-H_2SO_4$ gives a keto-acid (II), $C_{15}H_{24}O_3N_2$ [dihydrochloride,



m.p. 248° (decomp.); platinichloride, $+2H_2O$, m.p. 256°; diaurichloride, m.p. 211° (decomp.); Me ester dihydrochloride and diaurichloride, m.p. 202° (decomp.). HNO_3 gives $(CH_2 \cdot CO_2H)_2$. These and recorded data indicate the structures shown. Spartyrine is (IIIa) or (IIIb).

R. S. C.

Synthetic experiments in the benzylisoquinoline series. III. Laudanosoline 3':7-dimethyl ether from laudanosine. C. Schöpf and K. Thierfelder (Annalen, 1939, 537, 143—156; cf. A., 1932, 1040).—With 4.5 mols. of $AlCl_3$ in $PhNO_2$, first at 18—50° and then at 80—85°, laudanosine (I) is only partly changed and gives 8% of laudanone (hydro-

bromide, $+3\text{H}_2\text{O}$, sinters at 72° , m.p. $76-77^\circ$, loss of H_2O at $117-119^\circ$ (i.e., demethylation at C_{13}), which with Et_2SO_4 gives the Et ether ethosulphate and thence by NaOH crude 4:5:4'-trimethoxy-3'-ethoxy-2- β -methylethylaminoethylstilbene, m.p. $107-109^\circ$ (sinters at 100°), oxidised by O_3 to 3:4-OEt- $\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$ and 4:5-dimethoxy-2- β -methylethylaminoethylbenzaldehyde (II) [picrate, m.p. 185° (sinters at 182°)]. However, with 6 mols. of AlCl_3 (I) gives laudanoline 3':7-Me₂ ether, an oil [hydrobromide, $+ \text{H}_2\text{O}$, m.p. $175-176^\circ$ (sinters at 167°)], similarly degraded to 5:3'-dimethoxy-4:4'-diethoxy-2- β -methylethylaminoethylstilbene, m.p. $114-116^\circ$ (picrate, m.p. $193-194^\circ$), and thence to 4:3:1-OEt- $\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHO}$ and 5-methoxy-4-ethoxy-2- β -methylethylaminoethylbenzaldehyde (III) (picrate, m.p. $144-145^\circ$). Codamine, prepared from protopapaverine methohydroxide by H_2 -PtO₂ in EtOH at $50-55^\circ$, gives crude 4:3':4'-trimethoxy-5-ethoxy-2- β -methylethylaminoethylstilbene, m.p. $90-93^\circ$ (sinters at 82°), and thence 4-methoxy-5-ethoxy-2- β -methylethylaminoethylbenzaldehyde (picrate, m.p. $174-175^\circ$). ψ -Laudanine, prepared from norpapaverine methochloride by H_2 -PtO₂, gives 5:3':4'-trimethoxy-4-ethoxy-2- β -methylethylaminoethylstilbene, m.p. $110-111^\circ$, and thence (III) and 3:4-(OMe)₂ $\text{C}_6\text{H}_3\cdot\text{CHO}$. dl-6'-Bromolaudanoline (IV) (prep. by Br in aq. AcOH at 3°), m.p. 128° , gives 6'-bromo-4:5:3':4'-tetramethoxy-2- β -methylethylaminoethylstilbene, m.p. $128-129^\circ$, and thence 3:4:6:1-(OMe)₂ $\text{C}_6\text{H}_3\cdot\text{Br}\cdot\text{CHO}$ and (II). With AlCl_3 in PhNO_2 (IV) gives 6'-bromolaudanoline Me₂ ether [hydriodide, $+ \text{H}_2\text{O}$, sinters at $115-117^\circ$, double m.p. $133-134^\circ$ (decomp.) and 215°]. (?6'-)Chlorolaudanoline (prep. with difficulty), m.p. 131° , with 48% HBr gives (?) 6'-chlorolaudanoline hydrobromide, m.p. $100-105^\circ$ (decomp. 120°).

R. S. C.

Ergot alkaloids. V. Ergometrine, ergometrinine, ψ -ergotinine, ergocristine, and ergocristinine. A. KOFLER (Arch. Pharm., 1938, 276, 525-544; cf. A., 1938, II, 164).—The crystallo-optical properties of the many forms and solvates of the alkaloids named are described.

R. S. C.

Di(hydroxymethyl)dihydro-codeine and -morphine. C. MANNICH and K. SCHULTE (Arch. Pharm., 1938, 276, 593-596).—Dihydrocodeine, CH_2O , and $\text{Ca}(\text{OH})_2$ in aq. MeOH at room temp. give 7:7-di(hydroxymethyl)dihydrocodeine (I), hygroscopic, m.p. $110-113^\circ$ (Ac_2 derivative, m.p. 128°). 7:7-Di(hydroxymethyl)dihydromorphine, m.p. $282-283^\circ$ (decomp.) (Ac_4 derivative and its hydrochloride, amorphous), is similarly prepared and with CH_3N_2 in MeOH-Et₂O gives (I).

R. S. C.

Decomposition of alkaloids in aqueous solution. IX. Photochemical change of codeine and codeinone. R. DIETZEL and L. STADELMAN (Arch. Pharm., 1938, 276, 621-633; cf. B., 1934, 780).—Photochemical decomp. of codeine (I) involves oxidation, is independent of the solvent, but varies with the temp., not occurring at -3° . Acetylcodeine is stable. Codeinone (II) undergoes similar decomp., which, however, is independent of O_2 . Decomp. of (I) thus proceeds by way of (II), but attempts to isolate (II) from the products failed.

R. S. C.

Belladonnine. W. KÜSSNER (Arch. Pharm., 1938, 276, 617-620).—At 110° apotatropine gives belladonnine, $\text{C}_{34}\text{H}_{42}\text{O}_4\text{N}_2$, m.p. 129° (corr.) (sulphate; dihydrochloride, m.p. $\sim 195-196^\circ$), resistant to fission by acid, but converted by NaOH -aq. EtOH at 100° into β -isotropic acid and tropine.

R. S. C.

New synthesis of aromatic arsenic compounds. W. A. WATERS (Nature, 1938, 142, 1077).—Aromatic As compounds are formed by warming a diazonium chloride with powdered As and CaCO_3 under COMe_2 . PhN_2Cl yields a H_2O -sol. product from which AsPh_3S is pptd. by H_2S . Bi is attacked under similar conditions, but aromatic bismuthines are either not formed or are unstable under the conditions prevailing. Au yields AuCl_3 , but Tl is unattacked.

L. S. T.

Amides of β -p-arsonophenylpropionic acid. E. WALTON (J.C.S., 1939, 156-158).— β -p-Arsonophenylpropionic acid (Na salt), prepared from the NH_2 -acid, gives the Me ester (Na salt), which reacts with the appropriate amine to form β -phenylpropionamide- [Na salt ($+ \text{H}_2\text{O}$)], β -phenylpropionomethyl- (Na salt), -dimethyl- [Na salt ($+ \text{H}_2\text{O}$)], -ethyl- [NHEt_2 salt; Na salt ($+ 2\text{H}_2\text{O}$)], and -n-propyl-amide- [Na salt ($+ \text{H}_2\text{O}$)], -piperidide- (Na salt), and -anilide-p-arsinic acid (Na salt). These amides show some trypanocidal activity, but they are all more toxic than the analogues of the corresponding AcOH series.

F. R. S.

p-Acetyl- and p-phenacyl-oxyphenylarsinic acid.—See B., 1939, 216.

Arsonium compounds. II. F. F. BLICKE, H. H. WILLARD, and J. T. TARAS (J. Amer. Chem. Soc., 1939, 61, 88-90; cf. A., 1938, II, 166).—From AsR_3 and RHal at 100° are prepared: triphenyl-allyl-, m.p. $180-181^\circ$ (iodide, m.p. $163-164^\circ$), -p-nitrobenzyl-, m.p. $160-162^\circ$, -p-bromophenacyl-, m.p. $170-171^\circ$, Et_2 triphenylmalonate-, m.p. $169-171^\circ$, -arsonium bromide; triphenylbenzylarsonium iodide, m.p. $155-157^\circ$, and chloride, m.p. $180-181^\circ$; tribenzylallylarsonium bromide, m.p. $180-182^\circ$; diphenyl- α -naphthylbenzylarsonium iodide, m.p. $171-172^\circ$; and trisdiphenylallylarsonium bromide, m.p. $244-246^\circ$. None of these salts reacts quantitatively with I, ClO_4 , ReO_4 , or CdCl_4 . With AgNO_3 or conc. HNO_3 the halides give AsPh_4NO_3 , triphenyl-iodomethyl-, m.p. $189-190^\circ$, -benzyl-, m.p. $178-180^\circ$, -methyl-, m.p. $131-133^\circ$, - β -hydroxyethyl-, m.p. $138-140^\circ$, and -allyl-arsonium nitrate, m.p. $146-148^\circ$. Prep. of AsPh_4Cl is improved.

R. S. C.

Binary systems containing arsenic trichloride or 5-chloro-5:10-dihydrophenarsazine.—See A., 1939, I, 145.

Lipophilic chemotherapeutics. I. E. BERGMANN and R. HASKELBERG (J.C.S., 1939, 1-5).—In seeking a type of chemotherapeutic intended to have affinity to the lipins and not to the proteins, experiments in the introduction of "fatty" radicals into substances known to contain chemotherapeutically active groups, and synthesis of "fatty" substances containing chemically active groups not yet known to have any chemotherapeutical effect, are recorded. Quinine and cholesteryl formate (I) give a hydro-

chloride, m.p. 246—247° (decomp.), $[\alpha]_D^{25} +8.4^\circ$ in CHCl_3 , yielding a base, m.p. 150°, $[\alpha]_D^{25} -2.0^\circ$ in CHCl_3 . Similar condensation of the appropriate reagents affords *stearoylquinine hydrochloride*, m.p. 227—228° (decomp.); 1-benzeneazo-2-stearamidonaphthalene, m.p. 88°; substance, m.p. 196°, from benzeneazo- β -naphthylamine and (I); 4-benzeneazo-1-stearamidonaphthalene, m.p. 140.5°; compound, m.p. 193°, from (I) and benzeneazo- α -naphthylamine; N-palmitoyl- and -stearoyl-arsanilic acid; compound, decomp. 294°, from 4-arsonobenzeneazo- β -naphthylamine and palmitoyl chloride, and compound, m.p. 290° (decomp.), from the amine and (I); 4-cetyl-aminoazobenzene-4'-arsinic acid, m.p. 283° (decomp.); 1-4'-arsonobenzeneazo-2-octylaminonaphthalene, m.p. 206° (decomp.); 4-octylaminoazobenzene-4'-arsinic acid, m.p. 155° (decomp.); 6-methoxy-8-cholesteryl-carbamidoquinoline, m.p. 129°; 8-palmitamido-6-methoxyquinoline, m.p. 74—75°; compound, m.p. 232°, from (I) and 5-acrylaldehyde-p-ethylaminoanil, m.p. 210°; 5-(m-nitrostyryl)acridine methiodide, m.p. 232° (decomp.); N-nitroso-N-cholesterylaniline, m.p. 147.5°, from HNO_2 and cholesterylaniline; N-nitrosocetylaniline, m.p. 53°, from cetylaniline hydrochloride, m.p. 102°; and N-methyl-N-cetylaniline hydrochloride, m.p. 104°.

F. R. S.

Glyoxalines. VIII. Arsonophenylglyoxalines. R. WEIDENHAGEN and H. REINÄCKER (Ber., 1939, 72, [B], 57—67).— ω -Bromoacetophenone-p-arsinic acid (Elson and Gibson, A., 1931, 1316) is converted by boiling H_2O into ω -hydroxyacetophenone-p-arsinic acid, m.p. $>340^\circ$ (also $+1\text{H}_2\text{O}$); phenyl-hydrazone, m.p. $>400^\circ$, transformed by CH_2O , $\text{Cu}(\text{OAc})_2$, and NH_3 in boiling H_2O into 4(5)-p-arsonophenylglyoxaline ($+1\text{H}_2\text{O}$), m.p. 310° (decomp.) (Cu compound; nitrate). Under similar conditions MeCHO affords 4(5)-p-arsonophenyl-2-methylglyoxaline (I), decomp. $>300^\circ$ without melting, the Cu derivative of which is either converted by 10% HCl into the base hydrochloride ($+1\text{H}_2\text{O}$) which with NaOAc yields (I) or is treated successively with KI and NaH_2PO_2 and then oxidised (H_2O_2) to (I). By use of the requisite aldehyde the following 4(5)-p-arsonophenyl-glyoxalines are obtained; -2-ethyl-, m.p. 315° (decomp.) [Cu salt; hydrochloride, m.p. 275° (decomp.)]; -2-n-propyl-, m.p. 250° (decomp.) (also $+2.5\text{H}_2\text{O}$) (Cu salt; hydrobromide); -2-n-butyl-, decomp. 270° (Cu salt; nitrate); -2-n-hexyl-, needles, m.p. 195—197° (decomp.) after softening at 190°, or prisms, decomp. 256—260° (Cu salt; hydrochloride, decomp. 290°); 2-phenyl-, decomp. 330° (Cu salt; hydrochloride, decomp. 303°); 2-p-anisyl-, decomp. 310° (Cu salt; hydrochloride, decomp. 270°); -2-p-nitrophenyl-, m.p. 320—323° (decomp.) (Cu salt), which does not appear to yield a hydrochloride; -2-furyl-, decomp. 297° (Cu salt; hydrochloride); 2-p-carboxyphenyl-, m.p. 320° (decomp.) (Cu salt and unstable hydrochloride); α -p-hydroxy-m-carboxyphenyl-, gradual decomp. $>300^\circ$ [Cu salt; hydrochloride, m.p. 307° (decomp.)].

H. W.

Penta(acetoxymercuri)methylacetanilide. M. RAGNO (Gazzetta, 1938, 68, 738—740).— $\text{Hg}(\text{OAc})_2$ (5 mols.) and NPhMeAc (1 mol.) at 150—180° give 2 : 3 : 4 : 5 : 6-penta(acetoxymercuri)methylacetanilide,

decomp. 190—230°, which forms colloidal solutions in H_2O .

E. W. W.

Mercury derivatives of antipyrine. M. RAGNO (Gazzetta, 1938, 68, 741—747).—The compound $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_2\text{ClHg}$, from $\text{HgCl}\cdot\text{NH}_2$ and antipyrine (I) (A., 1921, i, 378), with 2 I gives iodoantipyrine. The product from (I) and $\text{Hg}(\text{OAc})_2$ (II) with HCl , KBr , and NaOH gives respectively the compounds, $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{ClHg}$, m.p. 95°, $\text{C}_{11}\text{H}_{11}\text{ON}_2\text{BrHg}$, m.p. 130°, and $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{Hg}$, m.p. 163°. In these compounds, Hg is apparently attached to a C. At 150°, (I) and (II) form dimercuriantipyrine diacetate, $\text{C}_{11}\text{H}_{10}\text{ON}_2(\text{HgOAc})_2$, m.p. 133°.

E. W. W.

Metallation as a side reaction in the preparation of organolithium compounds. H. GILMAN, W. LANGHAM, and A. L. JACOBY (J. Amer. Chem. Soc., 1939, 61, 106—109).— $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ (I) and Li in Et_2O give $\text{LiC}_6\text{H}_4\cdot\text{OMe}\cdot p$ (II) (evidenced by production of $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ by CO_2), but the reaction, $(\text{I}) + (\text{II}) \rightarrow \text{PhOMe}$ and $\text{LiC}_6\text{H}_4\text{Br}\cdot\text{OMe}\cdot 1 : 5 : 2$ [evidenced by production of $2 : 5 : 1\text{-OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$ (III) by CO_2], also occurs, particularly if the solution is heated under reflux. LiBu^a gives the same products. Li or LiBu^a and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OPh}$ give similarly $2 : 5 : 1\text{-OPh}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$, obtained also from PhOK and $5 : 2 : 1\text{-NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$ by way of $2 : 5 : 1\text{-OPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}_2\text{H}$ and $2 : 5 : 1\text{-OPh}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{CO}_2\text{H}$. However, $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ and $\text{LiC}_6\text{H}_4\text{Me}\cdot p$ give only $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ [and $\text{CO}(\text{C}_6\text{H}_4\text{Me}\cdot o)_2$] and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ (IV) [and $\text{CO}(\text{C}_6\text{H}_4\text{Me}\cdot p)_2$], respectively. Interaction of LiBu^a (1 mol.) with PhOMe (1 mol.) and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ (1 mol.) gives 30% of (III) and some (IV).

R. S. C.

Relative reactivities of organometallic compounds. XX. Metallation. H. GILMAN and R. L. BEBB (J. Amer. Chem. Soc., 1939, 61, 109—112; cf. A., 1938, II, 515).—3-Methoxydibenzfuran and LiBu^a give 60% of a 4 : 1 mixture of 3-methoxydibenzfuran-4- and -2-carboxylic acid. PhOMe gives the following yields of $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$: by LiBu^a in Et_2O 19, by NaBu^a in light petroleum 42, by NaPh in C_6H_6 44—64%. Ph_2O and CH_3CNa in liquid NH_3 give only a little $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$, and CPh_3Na has no effect; LiBu^a in light petroleum gives 7 and in Et_2O 60% of $o\text{-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Ph_2S gives similarly 24—56% of $o\text{-SPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Ph_2Se and LiBu^a give mainly SePhBu^a and LiPh , but a little PhSeH is also obtained. Only slight metallation of Ph_2 occurs. CH_2Ar_2 and LiBu^a give the following yields of $\text{CHAr}_2\cdot\text{CO}_2\text{H}$: CH_2Ph_2 20, $\text{CHPh}\cdot\text{C}_6\text{H}_4\text{Me}\cdot p$ 50, $\text{CH}_2\text{Ph}\cdot\text{C}_{10}\text{H}_7\cdot a$ 80%. $(\text{CH}_2\text{Ph})_2$ with NaBu^a or KBu^a gives $(\text{CHPh}\cdot\text{CO}_2\text{H})_2$, best in C_6H_6 , but LiBu^a gives only 1% of m - and p - $\text{Ph}[\text{CH}_2]_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. C_{10}H_8 gives 2.5 : 1 mixtures of α - and β - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$. Acenaphthene gives a mixture. 9 : 10-Dihydroanthracene and LiBu^a give 80% of 9 : 10-dihydroanthracene-9 : 10-dicarboxylic and 8% of the 9-carboxylic acid. Dibenzthiophen gives 23—90% of acid, the more reactive organometallic compounds causing also some dimetallation and the solvent also having considerable effect. Furan gives 7.5—40% yields of 2-furoic acid. By interaction of the Na salts with one another and with COPh_2 , the following order of

decreasing acidity is established: CPh:CH , $\text{C}_5\text{H}_{11}\text{:C:CH}$, C_2H_5 , $\text{C}_{16}\text{H}_{33}$ and cyclohexene are unaffected by LiBu^a . $\text{NaC}_5\text{H}_{11-n}$ and NPhMe_2 in light petroleum give $o\text{-NMe}_2\text{:C}_6\text{H}_4\text{:CO}_2\text{H}$. NaBu^a and HgPh_2 in light petroleum give 40% of BzOH , establishing the reaction, $\text{LiBu}^a + \text{HgPh}_2 \rightarrow \text{NaPh} + \text{HgPhBu}^a$. R. S. C.

Allylic rearrangements. VIII. Action of magnesium on cinnamyl chloride. W. G. YOUNG, G. BALLOU, and K. NOZAKI (J. Amer. Chem. Soc., 1939, 61, 12—15; cf. A., 1938, II, 214).—The Mg compound from $\text{CHPh:CH:CH}_2\text{Cl}$ is shown to contain 73% of MgCl:CHPh:CH:CH_2 and 27% of $\text{CHPh:CH:CH}_2\text{MgCl}$ by hydrolysis to $\text{CH}_2\text{Ph:CH:CH}_2$ and CHPh:CHMe (with coupling products and a little PhPr), followed by KMnO_4 -oxidation and determination of BzOH and AcOH . The Mg compound does not dissociate into MgCl and a resonating ion. R. S. C.

Analogous organic derivatives of sulphur, selenium, and tellurium. N. M. CULLINANE, A. G. REES, and C. A. J. PLUMMER (J.C.S., 1939, 151—153).—Diphenylene sulphide, prepared by diazotisation of 2-amidodiphenyl sulphide or from diphenylene selenide and S, with AcCl-AlCl_3 gives 3:6-diacetyldiphenylene sulphide, m.p. 210° , which with NaOH-CaOCl_2 affords diphenylenesulphone-3:6-dicarboxylic acid, m.p. above 400° . K selenophenoxide and $o\text{-C}_6\text{H}_4\text{:Cl:NO}_2$ yields 2-nitrodiphenyl selenide, reduced to the 2- NH_2 -compound; the diazotised amine with H_2SO_4 gives Ph_2 diselenide and benzene-seleninic acid. Diphenylene selenide can be obtained only in small yield under special conditions from this amine but can be prepared from selenanthren and Cu. Diphenylenesulphone and Te afford diphenylene telluride in small yield. F. R. S.

Natural organic high-molecular substances. K. FREUDENBERG (Naturwiss., 1939, 27, 17—22).—The formation (by continuous condensation processes), mol. size, and configuration of proteins, cellulose, rubber, lignin, tannins, etc. are discussed.

A. LI.

Phosphatide acid-protein compounds: chaulmoogroylglycerophosphate-protein compounds. T. WAGNER-JAUREGG and H. ARNOLD (Biochem. Z., 1938, 299, 274—280; cf. A., 1937, II, 365; 1938, II, 353).—The hydrochloride of clupein Me ester in H_2O with Na dichaulmoogroyl- β -glycerophosphate gives a H_2O -insol. compound (I) containing N 9.43, P 3.05%. ψ -Globulin (II) and albumin (III) from horse serum yield, in neutral or slightly acid solution, corresponding compounds with Na monochaulmoogroyl- β -glycerophosphate. The (II) compound has N 12.47, P 0.88% and contains 25—50 mols. of phosphatide acid per protein mol. and the (III) compound has P 0.93%. As regards pptn. with $(\text{NH}_4)_2\text{SO}_4$ the (II) compound behaves like euglobulin. Probably phosphatide acid-protein compounds are produced under physiological conditions. (I) appears to have no antigenic properties. (II) and (III) adsorb lactoflavinphosphoric acid but do not combine with it. W. McC.

Peptone derivatives of gelatin. II. Fractionation of the ereptic hydrolysate of gelatin-

peptone and -tryptone. III. Fractionation of gelatin-peptone and -tryptone. T. MORI (J. Biochem. Japan, 1938, 28, 333—343, 345—354; cf. A., 1939, III, 198).—II. Data for the total, NH_2 -, and arginine-N (the last being indicated by hydrolysis by arginase) of fractions obtained by the ereptic digestion of the peptone and tryptone are tabulated and discussed.

III. Data for the distribution of N, colour and pptn. reactions, and arginase hydrolysis of fractions obtained by pptn. of the aq. peptone and tryptone with phosphotungstic acid are tabulated and discussed. F. O. H.

Simplification of Pregl's method of determining carbon and hydrogen. K. BÜRGER (Ber., 1939, 72, [B], 40—45).—The chief modification consists in the attachment of the absorption tubes to the combustion tube and to one another by ground-glass joints instead of rubber stoppers. Considerable simplification of the apparatus and economy of time are thereby rendered possible. H. W.

Sub-micro-determination of nitrogen in organic material by Kjeldahl's method. C. DUMAZERT (Bull. Soc. Chim. biol., 1938, 20, 1405—1418).—A modification of the Parnas and Wagner micro-Kjeldahl apparatus by which 10—260 μg . of N can be determined with an error of 1% is described. Approx. 1 mg. of substance is heated for 2 hr. with 0.3 c.c. of H_2SO_4 and 10 mg. of a mixed catalyst prepared from 1 g. of HgSeO_3 and 24 g. of KHSeO_4 . A control is done at the same time. The NH_3 is liberated in the usual way and absorbed in 1 or 2 c.c. of 0.01N- H_2SO_4 . After addition of KI and KIO_3 , the liberated I is determined by 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$. J. N. A.

Determination of organic sulphur. G. H. YOUNG (Ind. Eng. Chem. [Anal.], 1938, 10, 686).—The method of Brunck (A., 1905, ii, 762) is of general applicability and is preferable to most other methods for the analysis of sulphones and sulphoxides. Details of apparatus and procedure are given.

F. N. W.

Microanalytical determination of mercury in organic and inorganic compounds. Accurate determination in presence of chlorine, bromine, iodine, nitrogen, and sulphur. M. BOËTIUS (J. pr. Chem., 1938, [ii], 151, 279—306).—For compounds free from N the combustion tube is drawn out at one end and into it are inserted successively a hollow glass cylinder-asbestos-Ag deposited on porcelain-asbestos-ignited PbO contained in a boat-substance-diffusion tube. For nitrogenous compounds the filling is hollow cylinder-Ag-asbestos-fine Cu-asbestos-granular PbCrO_4 -asbestos-substance-diffusion tube (combustion is effected in CO_2). The Hg is absorbed on fine threads of Au. H. W.

Chlorometric determination of the ethylene linking. L. PALFRAY and S. SABETAY (Ann. Chim. Analyt., 1938, [iii], 20, 288—289).—The sample (0.15—0.2 g.) is dissolved in CCl_4 , 25 c.c. of a solution containing ~ 1 g. of Cl_2 in 100 c.c. of CCl_4 are added, and the whole is well agitated and then kept in the dark for 30 min. KI is added and the liberated I titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ (starch). Results given

by this method with oleic and stearic acids and several oils are compared with those obtained by Hanus' method. L. S. T.

Quantitative separation of alcoholic substances. G. SANDULESCO and A. GIRARD (Compt. rend., 1938, 207, 874—876; cf. A., 1936, 1397).—Material (e.g., natural products) containing an alcohol (ROH) is treated with $(\text{CH}_2\text{Cl}-\text{CO})_2\text{O}$ (amount \propto Ac val.) in dioxan at 100° (bath)/3—4 hr. in absence of H_2O , the resulting product is freed from excess of anhydride and acid by aq. NaHCO_3 , and then heated with NEt_3 (or NMe_3) (10—20% excess) in dioxan at 100° (bath)/1—2 hr. (sealed tube). The $\text{NEt}_3\text{Cl}\cdot\text{CH}_2\text{CO}_2\text{R}$ thus formed is readily sol. in 10—20% AcOH , and treatment with NaOH at room temp. in presence of Et_2O gives the ROH. The method is applicable to phenolic alcohols provided the phenolic OH is first benzoylated (Schotten-Baumann). Cholesterol (1 g.) is separable from olive oil (1 litre), but is accompanied by (alcoholic) impurities. J. L. D.

New general reagent for enols; mercurous nitrate. IV. Interpretation of the reaction mechanism. E. V. ZAPPI and A. MANINI (Anal. Asoc. Quím. Argentina, 1938, 26, 89—105).—Pptn. of Hg by $\text{Hg}_2(\text{NO}_3)_2$ with enols and active substances is attributed to formation of complexes between the latter and $\text{Hg}(\text{NO}_3)_2$ with consequent disturbance of the equilibrium $\text{Hg}_2(\text{NO}_3)_2 \rightleftharpoons \text{Hg} + \text{Hg}(\text{NO}_3)_2$. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{-OH}$ with $\text{Hg}_2(\text{NO}_3)_2$ (1 mol.) gives Hg (1 mol.) and a cryst. complex, also obtained from $\text{Hg}(\text{NO}_3)_2$ without separation of Hg. $\text{C}_5\text{H}_5\text{N}$ similarly forms a complex, $2\text{C}_5\text{H}_5\text{N}\cdot\text{Hg}(\text{NO}_3)_2$, m.p. $246\text{—}248^\circ$. F. R. G.

Identification and determination of carbonyl by *p*-carboxyphenylhydrazine. S. VIEBEL and N. HAUGE (Bull. Soc. chim., 1938, [v], 5, 1506—1509).—A modified prep. of $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, and a method of determining CO by titration of hydrazone in EtOH against $\text{Ba}(\text{OH})_2$, are recorded. A. T. P.

Use of Lovibond Tintometer for colorimetric determination of formaldehyde by the phloroglucinol method. R. C. HOATHER and P. G. T. HAND (Analyst, 1939, 64, 29—30).—The $\text{C}_6\text{H}_3(\text{OH})_3$ reagent is added in varying quantity according to the CH_2O present. The Tintometer is set at 1.0 unit of brightness and observations of colour are made from 2 min. after mixing until the max. colour is passed (~4 min. longer). The p.p.m. of $\text{CH}_2\text{O} = (R - 1.2)/0.414t$, where R = red units and t = thickness of cell in inches. E. C. S.

Conductometric micro-titration of organic acids. M. FURTER and H. GUBSER (Helv. Chim. Acta, 1938, 21, 1725—1734).—The org. acid (5—30 mg.) is dissolved in aq. EtOH (10—14 c.c.) in a special conductivity cell in which the solution can be stirred by a stream of N_2 , and is titrated with 0.1N. aq. NaOH or LiOH from a micro-burette. Preferred concns. of solvents for mono-, di-, and poly-basic acids are 25—75%, 99%, and 80—95% EtOH , respectively. J. W. S.

Dyer method for identification and determination of volatile fatty acids. E. P. CLARK (J. G (A., II.)

Assoc. Off. Agric. Chem., 1938, 21, 684—688).—The consts. obtained by Dyer (A., 1917, ii, 157) relate to the conditions, not adequately specified, under which his observations were made. An accurately described apparatus is illustrated and a procedure detailed for the distillation, and the consts. so obtained for HCO_2H , AcOH , EtCO_2H , $\text{Pr}^n\text{CO}_2\text{H}$, and $\text{Pr}^s\text{CO}_2\text{H}$ are tabulated. The titrations are carried to a definite end-point by comparison with a buffered solution at p_H 8.6 of equal vol. E. C. S.

Schryver-Fosse reaction applied to analysis. M. PAGET and R. BERGER (Compt. rend., 1938, 207, 800—802).— $\text{H}_2\text{C}_2\text{O}_4$ (2 c.c.; 5—70 mg. per l.) when shaken with $n\text{-HCl}$ (1 c.c.) and Zn gives $\text{CHO}\cdot\text{CO}_2\text{H}$, which with $\text{NHPH}\cdot\text{NH}_2\cdot\text{HCl}$ at 100° followed by conc. HCl (1.8 c.c.) and 10-vol. H_2O_2 (2 drops) at room temp. gives a colour which is compared with a standard. 5 μg . can be identified. Ascorbic acid (1 c.c. of 0.1%) with conc. H_2SO_4 (2 drops)—3% of KMnO_4 (2 drops) at room temp. affords $\text{H}_2\text{C}_2\text{O}_4$ which is determined as above. 10—20 μg . can be determined. 0.1% aq. lactic, malic, citric, or tartaric acid is oxidised like ascorbic acid. Tartaric acid gives $\text{CHO}\cdot\text{CO}_2\text{H}$ (traces), $\text{H}_2\text{C}_2\text{O}_4$, and $\beta\gamma$ -diketobutane- $\alpha\delta$ -dicarboxylic acid. Most commercial samples of Na urate (or uric acid heated with Na_2CO_3) give the Schryver-Fosse reaction directly, owing to the presence of allantoinic acid. J. L. D.

Iodometric determination of small quantities of glucose. E. C. NOYONS (Rec. trav. chim., 1939, 58, 17—22).—The iodometric method (A., 1923, ii, 346) can be used to determine 0.2—2 mg. of glucose, after 30 min. oxidation at room temp. The accuracy is not greatly affected by the presence of various other substances found in blood. A glucose solution treated with $\text{Cd}(\text{OH})_2$ to remove albumin (A., 1932, 75) gives inaccurate results by this method unless buffered with $2\text{KH}_2\text{PO}_4 + 3\text{NaOH}$. E. W. W.

Micro-method for the determination of reducing sugars. I. A. OBERGARD, B. O. LJUBIN and A. J. TSCHULIATKOVA (Arch. sci. biol. U.S.S.R., 1935, 38, 343—352; Ger., 352—353).—The sugar is oxidised titrimetrically with a modified Fehling's solution (cf. A., 1932, 529) using methylene-blue as an internal indicator (cf. A., 1923, ii, 193; 1924, ii, 707). A conversion table is given. CH. ABS. (c).

Micro-determination of sugar alcohols. W. R. TODD, J. VREELAND, J. MYERS, and E. S. WEST (J. Biol. Chem., 1939, 127, 269—273).—0.1—0.7 mg. of the sugar is heated at 100° for 30 min. with $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Na}_2\text{SO}_4\text{-NaOH}$. After cooling $\text{ZnAc}_2\text{-KI-AcOH}$ is added and the liberated I is titrated. The titration val.-concn. curve is not linear and must be determined for each sugar. Sorbitol and mannitol are recovered to the extent of 95—110% from aq. solutions and 85—105% from blood and urine previously treated with HgSO_4 and BaCO_3 . A correction for the reducing action of glucose and its effect on the reducing power of sugar alcohol is described. J. L. D.

Use of drop analysis for investigation of medicaments. V. Detection of small quantities of primary aromatic amines. O. FREHDE and

K. FÜRST (Mikrochim. Acta, 1938, 3, 197—200; cf. A., 1938, II, 465).—The "mustard oil test" for aromatic amines is applied as a colour reaction by detecting by means of alkaline plumbite solution the H_2S liberated in the first stage of the test. Aliphatic amines do not react. The substance under investigation is mixed with 20 drops of EtOH-CS_2 (~0.02 g. in 50 c.c. of 96% EtOH), carefully evaporated in a special apparatus, and the vapour tested with paper moistened with alkaline plumbite solution. The limiting sensitivities given for the different amines tested in this way vary from 1.0 to 4.0 μg . L. S. T.

Determination of cholesterol. F. E. KELSEY (J. Biol. Chem., 1939, 127, 15—22).—The method described depends on the pptn. of cholesterol from $\text{EtOH-Et}_2\text{O}$ extracts of tissues as the digitonide, purification of this by light petroleum, decomp. by boiling C_6H_6 , and isolation of the free sterols by extraction with light petroleum. The product is assayed by the Liebermann-Burchard reaction. Where phospholipins are present, these must first be removed by COMe_2 pptn. Both free and total cholesterol can be determined on the same sample.

P. G. M.

Copper precipitation method for kojic acid determination. H. N. BARIAM (Ind. Eng. Chem. [Anal.], 1939, 11, 31—33; cf. A., 1938, II, 372).—The method is accurate if the solution to be analysed is neutralised and then diluted to ~0.142 g. of kojic acid in 70 c.c. before adding dil. aq. $\text{Cu}(\text{OAc})_2$ in >50% excess. At least 48 hr. are required for complete pptn.; the ppt. $(\text{C}_6\text{H}_5\text{O}_4)_2\text{Cu}$ is dried in vac. over CaCl_2 or at 100—105°. The p_{H} of the solution is not crit.

F. N. W.

Colorimetric determination of *dl*- α -tocopherol (vitamin-E). A. EMMERIE and C. ENGEL (Nature, 1938, 142, 873).—The determination is based on the reduction of FeCl_3 by α -tocopherol (I) in EtOH , the Fe^{2+} formed being determined colorimetrically by means of 2:2'-dipyridyl. The amounts of (I) varied from 0.01 to 0.4 mg. The results agree with those obtained by potentiometric titration with AuCl_3 (A., 1938, II, 450).

L. S. T.

Determination of free and combined pentoses in purine compounds. K. GERHARDT (Czasopismo Towarz. Apt. Lwow, 1936, 51, No. 9, 8 pp.; Chem. Zentr., 1937, i, 943).—The nos. quoted after the following compounds are respectively the max. yield of furfuraldehyde and the optimal $[\text{HCl}]$ (g. per 100 c.c.), when Hoffman's method (A., 1927, 687) is used: arabinose (80.4, 18.46), which is less readily decomposed than xylose (>80.4, 17.14); yeast (88.2, 17.89) and muscle (22.4—28.5, 16.66—18.33) adenine nucleotides.

H. B.

Determination of tryptophan by a modified glyoxylic acid method employing photo-electric colorimetry. J. L. D. SHAW and W. D. McFARLANE (Canad. J. Res., 1938, 16, B, 361—368).—Winkler's adaptation (A., 1934, 1376) of the Hopkins-Cole reaction is modified for use with a photo-electric colorimeter. 0.5 c.c. of Pesze's glyoxylic acid solution (A., 1936, 745) and 0.5 c.c. of 0.04N. aq. CuSO_4 are mixed with 0.1—2.0 c.c. of an aq. solution containing

0.005—0.150 mg. of tryptophan (I) and the mixture is made up to 3.0 c.c. with H_2O . 5 c.c. of conc. H_2SO_4 are added gradually, with cooling, and the mixture after 10 min. at room temp. and then 5 min. at 100° is cooled and made up to 10 c.c. with 60% H_2SO_4 . The colour developed is measured after 15 min. in an Evelyn colorimeter (*ibid.*, 1223) and the (I) content obtained from calibration curves. The method is applied to four samples of casein (II) by dissolution in 10—20% aq. NaOH or 5% aq. HCO_2H and it is shown that the age and origin of the (II) are factors causing variation in the (I) content.

F. N. W.

Iodometric determination of potassium mercuri-iodide; volumetric determination of morphine. H. WACHSMUTH (Bull. Soc. Chim. biol., 1938, 20, 1419—1428).— K_2HgI_4 is oxidised to KIO_3 by $\text{Br-H}_2\text{O}$, and after addition of KI and acid, the I is determined by 0.1N- or 0.05N- $\text{Na}_2\text{S}_2\text{O}_3$. For the determination of morphine, a slightly acid solution is treated with excess of K_2HgI_4 , and after removal of the ppt., the excess of K_2HgI_4 is determined in an aliquot of the filtrate. 0.01—0.03 g. of morphine can be determined even in presence of NaCl . Other methods of determination of morphine as its insol. mercuri-iodide are discussed.

J. N. A.

Stability of solutions of nicotindimethyl-amide. F. REMERS (Dansk Tidsskr. Farm., 1939, 13, 9—18).—Nicotinic acid is determined by extraction with $\text{CHCl}_3\text{-Pr}^n\text{OH}$ (3:1) at the isoelectric point [after first removing nicotindimethylamide (I)], followed by evaporation, dissolution in H_2O , and titration against 0.1N- NaOH (phenolphthalein). (I) is not hydrolysed in aq. solution (p_{H} 3—7.5) in 1 year at room temp. or by heating to 120°. The yellow colour of old solutions of (I) is probably due to a nitropyridylpyrazole.

M. H. M. A.

Determination of strychnine and brucine in mixtures of both. N. J. A. GROEN and P. VAN DER WIELEN (Pharm. Weekblad, 1939, 76, 3—10).—The method of the British Pharmacopoeia is preferred and gives satisfactory results for strychnine. The brucine is determined by Zeisel's OMe method.

S. C.

Volumetric determination of organic lead compounds. F. HEIN, A. KLEIN, and H. J. MESÉE (Z. anal. Chem., 1939, 115, 177—183).—In EtOH , PbEt_2 can be determined by direct titration with 0.1N-I (in EtOH), $\text{PbEt}_2 + \text{I}_2 = \text{PbEt}_2\text{I} + \text{EtI}$, until the yellow colour persists at least 15 min. If the determination is accelerated by addition of excess of I and back-titration with $\text{Na}_2\text{S}_2\text{O}_3$ or by warming secondary reactions occur. The reaction is more rapid in MeOH . A solution of PbEt_2 in petrol can be treated with excess of I in petrol, and back-titrated with aq. $\text{Na}_2\text{S}_2\text{O}_3$. After addition of MeOH titration may also be carried out directly with I in MeOH . PbEt_2 can be determined by direct titration with I in MeOH solution: $2\text{PbEt}_2 + \text{I}_2 = 2\text{PbEt}_2\text{I}$. PbPh_4 in C_6H_6 is treated with excess of I (in C_6H_6), reaction being accelerated by warming almost to the b.p. and irradiating with light. Reaction occurs: $\text{PbPh}_4 + 3\text{I}_2 = \text{PbI}_2 + 4\text{PhI}$. The excess of I is finally titrated with aq. $\text{Na}_2\text{S}_2\text{O}_3$.

J. W. S.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1939.

Hydrocarbon, $C_{28}H_{58}$, m.p. 63° , and acid, $C_{18}H_{36}O_2$, m.p. 55° , from cow's pregnancy urine.—See A., 1939, III, 144.

Influence of substituents on additive reactivity of ethylene derivatives.—See A., 1939, I, 206.

Oxidation of ethylenic hydrocarbons by selenious anhydride. A. GUILLEMONAT (Ann. Chim., 1939, [xi], 143—211; cf. A., 1936, 51; 1937, II, 405; 1938, II, 268).—The oxidation is effected by the gradual addition of finely divided SeO_2 to a solution of the hydrocarbon in $AcOH-Ac_2O$. With hydrocarbons $CRMe:CHMe$ a considerable proportion of the initial material always remains. Oxidation occurs at the most substituted C atoms vicinal to the C having the ethylenic linking, thus giving

$OH\cdot CHR\cdot CMe:CHMe$ where R may be H. The radicals form the series $CH_2\cdot$, Me, $CH\cdot$ in order of decreasing facility of oxidation; this effect is so marked that one product usually results in overwhelming proportion, e.g., $CMeEt:CHMe$ gives 34% of $OH\cdot CHMe\cdot CMe:CHMe$ and only 1% of $OH\cdot CH_2\cdot CMe:CHMe$, and $CMe_2:CHEt$ gives only $OH\cdot CH_2\cdot CMe:CHEt$. Steric influences appear without effect since $CMeBu^t:CHMe$ and $CPhEt:CHMe$ afford $OH\cdot CH_2\cdot CBu^t:CHMe$ and $OH\cdot CHMe\cdot CPh:CHMe$ in good yield. $CMe_2:CHMe$ is oxidised to β -methyl- Δ^2 -butenyl acetate, b.p. $148-150^\circ$, hydrolysed $[Ba(OH)_2]$ to β -methyl- Δ^2 -buten- α -ol, b.p. $136-138^\circ$, identified by hydrogenation to $CHMeEt\cdot CH_2\cdot OH$ and by oxidation to tiglaldehyde, b.p. $114-118^\circ$ (semicarbazone, m.p. 225°).

$CMeEt:CHMe$ yields β -acetoxy- γ -methyl- Δ^2 -pentene, b.p. $57-59^\circ/19$ mm., hydrolysed to γ -methyl- Δ^2 -penten- β -ol, b.p. $54-56^\circ/18$ mm., and γ -acetoxy-methyl- Δ^2 -pentene, b.p. $65-67^\circ/19$ mm., hydrolysed to γ -hydroxymethyl- Δ^2 -pentene, b.p. $149-150^\circ/760$ mm., oxidised to the corresponding aldehyde (semicarbazone, m.p. 198° ; *p*-nitrophenylhydrazone, m.p. $154-155^\circ$). β -Bromo- γ -methyl- Δ^2 -pentene, b.p. $62-64^\circ/32$ mm., from the corresponding alcohol and PBr_3 , is transformed by $MgMeBr$ into β - γ -dimethyl- Δ^2 -pentene, b.p. $91^\circ/760$ mm., oxidised by SeO_2 to unchanged material possibly containing a little β - γ -dimethyl- Δ^2 -pentadiene, and β -isopropyl- Δ^2 -butenyl acetate, b.p. $75-77^\circ/28$ mm., hydrolysed to β -isopropyl- Δ^2 -buten- α -ol, b.p. $65-67^\circ/24$ mm.; this is reduced (Adams) to β -isopropylbutyl alcohol and oxidised to α -isopropylbutaldehyde (semicarbazone, m.p. 125°). $CMeBu^t:CHMe$ yields β -tert.-butyl- Δ^2 -butenyl acetate, b.p. $82^\circ/22$ mm., hydrolysed to β -tert.-butyl- Δ^2 -buten- α -ol, b.p. $82^\circ/22$ mm., which affords $MeCHO$ when ozonised. β -Methyl- Δ^2 -pentene gives β -methyl- Δ^2 -pentenyl acetate, b.p. $61-63^\circ/12$ mm., whence β -methyl- Δ^2 -penten- α -ol, b.p. $61-63^\circ/14$ mm.,

identical with the product of the reduction of methyl-ethylacetaldehyde. γ -Phenyl- Δ^2 -pentene, b.p. $87-89^\circ/17$ mm., obtained by dehydration of $CPhEt_2\cdot OH$ derived from $EtOBz$ and $MgEtBr$, is oxidised to β -acetoxy- γ -phenyl- Δ^2 -pentene, b.p. $127-130^\circ/20$ mm., hydrolysed to γ -phenyl- Δ^2 -penten- β -ol, b.p. $122^\circ/18$ mm.

In the case of cyclic hydrocarbons with a double linking in the ring, oxidation results in the replacement by OH of H attached to C in the α -position to the double linking and always occurs in the ring if there is a possibility of oxidation. In consequence of dehydration of the *tert.* alcohol formed initially, the oxidation of CH leads to a diene with conjugated double linkings; these are also produced by oxidation of hydrocarbons with a cyclic, di-*tert.* double linking. Ethyl- Δ^1 -cyclohexene is oxidised to 2-ethyl- Δ^2 -cyclohexenyl acetate, b.p. $89-90^\circ/15$ mm., hydrolysed to 2-ethyl- Δ^2 -cyclohexen-1-ol, b.p. $82-83^\circ/12$ mm., which is oxidised to 2-ethyl- Δ^2 -cyclohexenone, b.p. $78-80^\circ/15$ mm. (semicarbazone, m.p. 175°). Ethyl- Δ^1 -cyclopentene, b.p. $105-106^\circ$, gives 2-ethyl- Δ^2 -cyclopentenyl acetate, b.p. $75-77^\circ/20$ mm., whence 2-ethyl- Δ^2 -cyclopentenol, b.p. $74-75^\circ/20$ mm., oxidised to 2-ethyl- Δ^2 -cyclopentenone, b.p. $78^\circ/27$ mm. (semicarbazone, m.p. 190°). 1-Methyl- Δ^1 -cyclohexene is oxidised to 2-methyl- Δ^2 -cyclohexenol, which is converted by PBr_3 into 1-bromo-2-methyl- Δ^2 -cyclohexene, b.p. $78-79^\circ/26$ mm., transformed by $MgMeBr$ into 1:2-dimethyl- Δ^2 -cyclohexene, b.p. $130-131^\circ/768$ mm. This is oxidised by SeO_2 to *o*-xylene and 2:3-dimethyl- $\Delta^{1:3}$ -cyclohexadiene (I), hydrogenated to 1:2-dimethyl- Δ^1 -cyclohexene (II) and transformed by maleic anhydride into the adduct, $C_{12}H_{16}O_3$, m.p. $122-123^\circ$. (II), b.p. $135-137^\circ/760$ mm., is oxidised to (I), further identified by condensation with $(i-CO_2Me)_2$ to Me_2 4:5-dimethyl-1:4-endoethylene-1:4-dihydrophthalate, pyrolysed to C_6H_4 and an ester hydrolysed to 4:5:1:2- $C_6H_2Me_2(CO_2H)_2$.

Oxidation of aliphatic hydrocarbons with a di-*sec.* double linking occurs generally to only a slight extent and gives very little identifiable product. Little or no pptn. of Se occurs. Oxidation occurs at the C in the α -position to the double linking. CH_2 is more readily oxidised than Me. A double linking at the end of a chain is as active as a di-*sec.* double linking but in consequence of rearrangement a primary and not a *sec.* alcohol is obtained. If radicals CH_2 are present on each side of the ethylenic carbons, both radicals are oxidised and mixtures of alcohols are obtained which may become complicated further as a consequence of rearrangements. Δ^2 -Pentene is oxidised to β -acetoxy- Δ^2 -pentene, b.p. $135-137^\circ$, hydrolysed to Δ^2 -penten- β -ol, b.p. $118-121^\circ$, which is hydrogenated (Adams) to pentan- β -ol, b.p. $116-118^\circ$.

Δ^{α} -Hexene is transformed into Δ^{β} -hexenyl acetate, b.p. 165—170°, hydrolysed to Δ^{β} -hexen- α -ol, b.p. 156°. Oxidation of Δ^{δ} -nonene gives an acetate, b.p. 89—91°/15 mm., giving a nonenol, b.p. 85—87°/11 mm., hydrogenated to a nonanol, b.p. 90—91°/18 mm.; since a cryst. derivative of this alcohol could not be obtained it is probable that the product is a mixture. Similarly, Δ^{γ} -nonene appears to yield mixtures of nonenyl acetates, b.p. 99—100°/17 mm., nonenols, b.p. 93—95°/15 mm., and nonanols, b.p. 93°/17 mm. Cyclic hydrocarbons with doubly linked *tert.* C are somewhat less readily oxidised than those with a *di-sec.* ethylenic linking but give yields of the order 30—40%; the general behaviour is similar to that of the corresponding aliphatic compounds. Thus *cyclohexene* yields Δ^2 -*cyclohexenyl acetate*, b.p. 68—70°/15 mm., hydrolysed to Δ^1 -*cyclohexen-1-ol* (phenylurethane, m.p. 106.5—107.5°). 3-Methyl- Δ^1 -*cyclohexene*, b.p. 102°/760 mm., yields 4-methyl- Δ^2 -*cyclohexenyl acetate*, b.p. 88—90°/20 mm., hydrolysed to 4-methyl- Δ^2 -*cyclohexen-1-ol*, b.p. 65—66°/6 mm. [identified by hydrogenation to 4-methylcyclohexanol, b.p. 169°/760 mm. (phenylurethane, m.p. 122°)], and 2-methyl- Δ^5 -*cyclohexenyl acetate*, b.p. 82—84°/17 mm., hydrolysed to 2-methyl- Δ^5 -*cyclohexenol*, b.p. 72—74°/15 mm. [identified by oxidation to 2-methyl- Δ^5 -*cyclohexenone*, b.p. 70°/15 mm. (semicarbazone, m.p. 178—180°)]. 4-Methyl- Δ^1 -*cyclohexene* is oxidised to a mixture of the acetates of 6-, 4-, and 5-methyl- Δ^2 -*cyclohexenol*.

The possibility that selenides are intermediate products of the reaction is established by the isolation of isoprene, tiglaldehyde, tiglic acid, and *di- β -methyl- Δ^{β} -butenyl selenide*, b.p. 97°/8 mm., by the action of SeO_2 on $\text{CHMe}:\text{CMe}_2$ in C_6H_6 at room temp.; this is characterised by the ppts. it gives with $\text{H}_2\text{Fe}(\text{CN})_6$ and with HgCl_2 , by conversion by O_3 into Se and MeCHO , and by pyrolysis under atm. pressure into Se, isoprene, and $\text{CHMe}:\text{CMe}_2$ and their polymerides and by pyrolysis in AcOH into Se and tiglyl alcohol. The Raman spectra of most of the substances mentioned are recorded. H. W.

Composition of primary polymerisation products of propene and the butenes. H. HOOG, J. SMITTEBERG, and G. H. VISSER (II Congr. mond. Pétrole, 1937, 2, 489—495).—Propene, Δ^{α} , Δ^{β} , and *iso*-butene were polymerised under mild conditions by passage over a solid H_3PO_4 catalyst, the olefine polymerides were hydrogenated, and the resulting paraffins analysed. It is concluded that quaternary C do not take part in the polymerisation, but a re-grouping may occur which will produce a *tert.* C. Couplings between similar C occur only to a slight degree, if at all. Coupling between *tert.* and primary C takes preference of any other possible combination. These conclusions may not be valid at high temp., which promote secondary reactions. R. B. C.

Spectroscopic and chemical study of aliphatic terpenes. V. Hydrocarbons derived from aliphatic alcohols. G. DUPONT, R. DULOU, and V. DESREUX (Bull. Soc. chim., 1939, [v], 6, 83—91; cf. A., 1936, 1514; 1938, II, 80).—Raman spectra of the products show that reduction (NaNH_2 in liquid NH_3) of β -geraniol or β -linalool, or ($\text{Na} + \text{EtOH}$) of

myrcene, yields only β -methylgeraniolene. Cyclisation (AcOH —50% H_2SO_4) of this yields chiefly α -methylcyclogeraniolene (A., 1926, 1238), whilst dehydration (anhyd. $\text{H}_2\text{C}_2\text{O}_4$) of dihydrolinalool (I) yields the ϵ -, α -, and γ -isomerides in the ratio 5 : 3 : 2, as shown by the Raman spectrum and the results of ozonolysis and of partial hydrogenation (Raney Ni). Dehydration (HPO_3 or hydrated $\text{H}_2\text{C}_2\text{O}_4$) of (I) gives mixtures of aliphatic dienes with cyclic compounds.

A. L.

Rate of the haloform reaction.—See A., 1939, I, 205.

Trichloro-bromo- and -iodo-methane. J. H. SIMONS, T. K. SLOAT, and A. C. MEUNIER (J. Amer. Chem. Soc., 1939, 61, 435—436).— $\text{CCl}_3\cdot\text{COBr}$ (prep. in 70% yield from $\text{CCl}_3\cdot\text{COCl}$ by HBr at $<0^\circ$) at 400° gives 10% of CCl_3Br and 5% of C_2Et_6 . Distillation/1 atm. of $\text{CCl}_3\cdot\text{COI}$ gives 75% of CCl_3I and 5% of C_2Et_6 . $\text{CCl}_3\cdot\text{COCl}$ at 600° gives CCl_4 (10 parts), C_2Et_6 (1 part), CO , and COCl_2 . Anhyd. $\text{CCl}_3\cdot\text{CO}_2\text{Na}$ and $\text{CCl}_3\cdot\text{CO}_2\text{Hg}$ do not react with Br , even at high temp. CCl_3Br and CCl_3I form at most traces of Mg derivatives. R. S. C.

Stabilised carbon tetrachloride.—See B., 1939, 240.

Promoter effect of platinic chloride on Raney nickel.—See A., 1939, I, 208.

Manufacture of alkali alkoxides.—See B., 1939, 241.

Alkyl carbonates.—See A., 1939, I, 190, 206.

Vapour-phase catalytic conversion of methyl-*tert.*-butylcarbinol and *tert.*-butylethylene. P. L. CRAMER and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1939, 61, 230—232).—When passed over activated Al_2O_3 at 310° and 390°, $\text{CHMeBu}^\gamma\text{OH}$ (I) gives $\text{CH}_2:\text{CHBu}^\gamma$ (II) 64.2 and 61.5, $\text{CHMe}:\text{CHPr}^\beta$ (III) 28.2 and 21.6, and $(\text{CMe}_2)_2$ (IV) 7.6% and a trace, respectively. When passed over $\text{Al}_2(\text{SO}_4)_3$ at 275°, (I) or (II) gives (II) 3.5, (III) 34, and (IV) 62.5%. (II) is unaffected by Al_2O_3 at 350°. Thus, rearrangement during dehydration of (I) by acids is due to rearrangement of the (II) primarily formed. R. S. C.

A $\beta\delta$ -diene alcohol. C. K. HOVO (Compt. rend., 1939, 208, 40—42).— $\text{CH}_2:\text{CH}\cdot\text{CHO}$ and Mg allyl bromide afford (35%) vinylallylcarbinol, converted by PBr_5 into a desmotropic mixture, b.p. 52—57°/17 mm., of γ -bromo- $\Delta^{\alpha\alpha}$ - and α -bromo- $\Delta^{\beta\alpha}$ -hexadiene; this with NaOAc — AcOH or NaOAc — EtOH affords (80%) α -acetoxy- $\Delta^{\beta\alpha}$ -hexadiene, b.p. 68—70°/14 mm., hydrolysed (EtOH — KOH) to *hexa- $\Delta^{\beta\alpha}$ -dien- α -ol*, b.p. 71—72°/14 mm., which when heated (sealed tube) with dil. EtOH — KOH at 180° gives *hexa- $\Delta^{\beta\delta}$ -dien- α -ol*, b.p. 77—78°/14 mm. J. L. D.

Linalool. Isomerisation of linalool by heating under pressure. I. Plinol. II. *iso*Plinol. T. IKEDA and K. WAKATSUKI (J. Chem. Soc. Japan, 1936, 57, 425—435, 435—441).—I. Linalool heated under N_2 at 250°/200 atm. for several hr. and then distilled yields in the final fraction the *tert.* alcohol, *plinol* (I), $\text{C}_{10}\text{H}_{18}\text{O}$, m.p. 94°, b.p. 209° (phenylurethane, m.p. 118°), which is dehydrated to the diene *plinolene* (II), $\text{C}_{10}\text{H}_{16}$. Hydrogenation (Pd) of (I) gives

dihydroplinol and of (II) *tetrahydroplinolene*. Decomp. of the ozonide of (I) furnished CH_2O , HCO_2H , and a ketone (III), $\text{C}_9\text{H}_{14}\text{O}$ (*semicarbazone*, m.p. 158°), hydrogenated to the saturated ketone, $\text{C}_9\text{H}_{16}\text{O}$ (*semicarbazone*, m.p. 178°); with H_2O the ozonide of (I) gave a saturated ketoglycol, $\text{C}_9\text{H}_{16}\text{O}_3$, m.p. 166° . (III) may be reduced to a H_2 -derivative and this oxidised to acids, $\text{C}_6\text{H}_{10}\text{O}_2$ and $\text{C}_8\text{H}_{14}\text{O}_2$.

II. The mother-liquor from the prep. of (I) yields the *tert.* alcohol isoplinal (IV), m.p. 41° (*naphthylurethane*, m.p. 130°), by oxidising with CrO_3 , removing citral, and distilling the residual unattacked oil. (IV) is dehydrated to isoplinalene and contains no 6-membered ring as it is not dehydrogenated by S or Se, but (IV) is reduced to *dihydroisoplinal* and (V) to *tetrahydroisoplinalene*. Decomp. of the ozonide of (IV) gives CH_2O and HCO_2H , indicating a :CH_2 group, and a ketone, $\text{C}_9\text{H}_{14}\text{O}$ (*semicarbazone*, m.p. 157.5°), hydrogenated to the saturated ketone, $\text{C}_9\text{H}_{16}\text{O}$ (*semicarbazone*, m.p. 179.5°), oxidised to (KMnO_4) the acids $\text{C}_6\text{H}_{10}\text{O}_2$ and $\text{C}_7\text{H}_{12}\text{O}_2$ or $\text{C}_8\text{H}_{14}\text{O}_2$. CH. ABS. (c)

Constitution of linoleyl alcohol prepared by sodium reduction of linoleic acid. J. P. KASS, E. S. MILLER, and G. O. BURR (J. Amer. Chem. Soc., 1939, 61, 482–483).—Linoleyl alcohol, obtained from Me linoleate by Na–BuOH, is shown to be a mixture of $\Delta^{\mu-}$ and $\Delta^{\mu-}$ -octadien- α -ol by its adsorption spectrum (max. at 2300–2350 \AA , $E_{1\text{cm}}^{1\%}$ 600), oxidation by KMnO_4 in COMe_2 to hexoic, azelaic, and sebacic acids, and physical data recorded in the lit.

R. S. C.

Lano-octadecyl alcohol, $\text{C}_{18}\text{H}_{38}\text{O}$, m.p. $42\text{--}43^\circ$ (*phenylurethane*, m.p. $79.5\text{--}80^\circ$), and **lanil alcohol**, $\text{C}_{21}\text{H}_{42}\text{O}_2$, m.p. $79.5\text{--}80^\circ$ (*bisphenylurethane*, m.p. 97°), from wool wax.—See A., 1938, III, 1018.

α -Naphthylcarbamic esters of complex aliphatic alcohols and their fission by methylalcoholic potassium hydroxide. J. TISCHER (Ber., 1939, 72, [B], 291–297).—Complex primary alcohols with an even no. of C give α -naphthylcarbamates hydrolysed by KOH–MeOH in 60–80 min. to the corresponding alcohol, $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$, and a little $\text{CO(NH}\cdot\text{C}_{10}\text{H}_7)_2$. Under similar conditions urethanes of complex primary alcohols with an odd no. of C yield also a considerable amount of $\text{C}_{10}\text{H}_7\text{-NH}\cdot\text{CO}_2\text{Me}$. α -Naphthylurethanes of complex *sec.* alcohols are formed with much greater difficulty and are much more resistant to alkaline hydrolysis. A differentiation of the different classes of alcohol along these lines is suggested. The following are new: *pentadecyl*, m.p. $84.5\text{--}85^\circ$ (corr.), *heptadecyl*, m.p. 88.5° (corr.), “*myricyl*,” m.p. $80\text{--}94.5^\circ$, and *di-n-hexylcarbinyll*, m.p. $50\text{--}51^\circ$, α -naphthylcarbamate. H. W.

Partly O-methylated hexitols. I. 1:2:3:5:6-O-pentamethyl-d-sorbitol. P. A. LEVENE and M. KUNA (J. Biol. Chem., 1939, 127, 49–53).—Nonamethyl- β -4-glucosidosorbitol (cf. A., 1937, II, 318) with 5% HCl at 100° under pressure affords a product which when oxidised (Willstätter–Schudel) yields 1:2:3:5:6-O-pentamethylsorbitol, b.p. $128\text{--}133^\circ/3\text{ mm.}$, $[\alpha]_D^{25} -10.1^\circ$ in EtOH, and $\alpha\beta\gamma\epsilon$ -tetramethyl- δ -d-gluconolactone. J. L. D.

Non-reaction of ethylene oxide and methanol. J. L. JONES (J. Amer. Chem. Soc., 1939, 61, 527–528).— $(\text{CH}_2)_2\text{O}$ and MeOH do not react, at least at $<350^\circ$. This indicates a very small steric factor and high activation energy. The liquid-phase reaction must then be ionic. R. S. C.

Reaction of aliphatic ethers with Denigès' reagent. E. M. MARKS and D. LIPKIN (J. Org. Chem., 1939, 3, 598–602).—None of the straight-chain ethers examined appears to react with Denigès' reagent, the no. of C and the position of O in these compounds being seemingly without influence. Compounds containing Bu γ are reactive. Bu γ OH and MeOBu γ become opaque within 4 min., replacement of OH by OMe not affecting the rate of change. EtOBu γ is somewhat less reactive and examination of PrOBu γ and Bu α OBu γ shows that further lengthening of the straight-chain radical increases this effect greatly. Pr α OBu γ is highly reactive. Compounds containing the *tert.*-amyl radical behave like Bu γ compounds except that their rates of reaction are usually slower and they ultimately give white needle like ppts. instead of yellow, curdy deposits; the two classes of compounds may possibly be thus differentiated. Replacement of OH by OAlk in *tert.*-amyl alcohol causes a greater lowering of the reaction rate than that shown in the Bu γ series. EtOBu β does not react with Denigès' reagent. Apparently the primary C connecting the O with the branched part of the Bu retards the change considerably.

$(\text{CH}_2)_2\text{CMe}\cdot\text{CH}_2)_2\text{O}$ is quite reactive probably by reason of the unsaturation within the mol. since a fully saturated ether with a similar structure should be quite inert towards the reagent. H. W.

Mechanisms for the rearrangements of ethers. Phenyl γ -ethylallyl [Δ^{β} -pentenyl] and vinyl γ -ethylallyl ether. C. D. HURD and M. A. POLLACK (J. Org. Chem., 1939, 3, 550–569).—Ozonisation followed by hydrolytic oxidation with H_2O and Ag_2O of $\text{CHEt}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (I), $\text{CHEtCl}\cdot\text{CH}\cdot\text{CH}_2$ (II), and $\text{CHMeCl}\cdot\text{CH}\cdot\text{CHMe}$ (III) gives respectively EtCO_2H , HCO_2H , and AcOH , separable by steam-distillation from the concurrently formed $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{OH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. In the steam distillate HCO_2H is determined by oxidation with CrO_3 ; EtCO_2H and AcOH are distilled off and the aq. distillate is analysed by the Duclaux method. Further in the latter mixture EtCO_2H is oxidised quantitatively to C_2O_4 by hot, alkaline KMnO_4 , leaving AcOH which is distilled off and identified by the Duclaux vals. and by conversion into *p*-bromophenacyl acetate. Analysis of the chloropentenes obtained by the method of Lauer and Filbert (A., 1936, 1244) shows the fraction of higher b.p. (IV), assumed to be pure (I), to contain 89% of (I), 11% of (II), and only a trace of (III). The fraction of lower b.p., assumed to be pure (II), is composed of 62% of (II), 36% of (I), and 2% of (III). Condensation of (IV) with PhOH gives a mixture of Ph pentenyl ethers shown by ozonolysis to consist of 90% of Ph Δ^{β} -pentenyl ether and 10% of Ph α -vinylpropyl ether. The rearrangement product formed by heating this mixture contains 56% of α - α -vinylpropylphenol from the normal γ -rearrange-

ment, 42% of the isomeric *o*- α -methyl- Δ^8 -butenyl-phenol from the abnormal rearrangement, and a small amount of *o*- Δ^8 -propenylphenol.

A mixture of pentenyl bromides (81.5% of $\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CH}_2\text{Et}$ and 18.5% of $\text{CH}_2\cdot\text{CH}\cdot\text{CHBrEt}$) is condensed with $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{ONa}$ to β -hydroxyethyl pentenyl ether, b.p. 85–87°/13 mm., converted by PBr_3 and anhyd. $\text{C}_5\text{H}_5\text{N}$ into β -bromoethyl pentenyl ether, b.p. 79°/11 mm., and thence by KOH at 160–170° into vinyl pentenyl ether (V), b.p. 97–101°/atm. pressure. (V) is assumed to be a mixture of $\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Et}$ and $\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ in the ratio 81.5:18.5. It is readily hydrolysed to MeCHO and pentenyl alcohol. Its thermal stability is about the same as that of $\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$. Short heating of the vapours at ~255° gives a 35% conversion into heptenaldehyde (VI) whereas practically complete conversion is effected in a sealed tube at 220°. Ozonolysis of (VI) yields HCO_2H , EtCO_2H , and AcOH in the mol. ratio 76.5:18.9:4.6, thus indicating that (VI) is a 76.5:18.9:4.6 mixture of β -ethyl- Δ^7 -pentenal, Δ^7 -heptenal, and β -methyl- Δ^7 -hexenal. Thus the abnormal effect which is so prominent in the case of $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Et}$ also results but to a much smaller extent with $\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Et}$. The various mechanisms which have been proposed to account for the rearrangement of ethers are examined critically. It is suggested that the initial effect of heat on the system $\text{C}\cdot\text{C}\cdot\text{O}\cdot\text{C}\cdot\text{C}\cdot\text{C}$ is to alter the position of the pair of electrons which bind the allyl group to O so that a semi-ionisation occurs. Actual separation into ions does not occur but the semi-ionisation promotes other ionic disturbances at the double linkings. This effect, combined with the spatial proximity of the atoms at the end of the systems, brings about temporary ring-closure and readjustment of electrons. The mechanism explains the intramol. nature of the reaction and the inversion of the "wandering" radical. The semi-ionic positive C seeks to satisfy its electron deficiency by appropriating electrons from the neighbouring double linking. This process is reversible but the next step which involves cyclisation is irreversible. Two mechanisms are suggested for the explanation of *para* rearrangements.

H. W.

Ether-like compounds. XXII. Synthesis of ether acetals by aid of γ -halogeno-ethers. M. H. PALOMAA and T. K. KASKI (Ber., 1939, 72, [B], 317–318).—Protracted heating of $\text{CH}(\text{OEt})_3$ with a solution of $\text{OMe}[\text{CH}_2]_3\text{MgCl}$ in C_6H_6 or PhMe gives γ -methoxybutaldehyde *Et*₂ acetal, b.p. 71–74°/5–6 mm., in about 18% yield.

H. W.

Synthesis of γ -methylthiolpropyl alcohol ("methionol"). S. AKABORI and T. KANEKO (Bull. Chem. Soc. Japan, 1939, 14, 1–2).—Allyl alcohol and MeSH react (varying time periods) in air, O_2 , or H_2 , in presence of $\text{Hg}(\text{SMc})_2$, in a sealed tube, to give $\text{SMc}[\text{CH}_2]_3\text{OH}$. The yield is 93% in O_2 at room temp. for one month; in H_2 there is no reaction in diffused light, but some occurs in the dark. The use of $\text{Hg}(\text{OAc})_2$ as catalyst in air at 140–160° affords a 61% yield of the alcohol (cf. Kirner, A., 1928, 1214).

A. T. P.

Instability of ammonium salts of higher fatty acids. J. E. KENCH and T. MALKIN (J.C.S., 1939, 230–232).—Interaction of fatty acids (C_{10} – C_{18}) and NH_3 in EtOH yields the NH_4 salts, which rapidly lose NH_3 , giving the acid NH_4 salts, $\text{RCO}_2\text{NH}_4\cdot\text{RCO}_2\text{H}$, which are formed directly from the acid and NH_3 in Et_2O . The following m.p. data are recorded: NH_4 H heptate, m.p. 45°, octate, m.p. 54°, decate, m.p. 68°, undecate, m.p. 72°, laurate, m.p. 77°, tridecate, m.p. 81°, myristate, m.p. 84°, pentadecate, m.p. 86°, palmitate, m.p. 89°, margarate, m.p. 91°, stearate, m.p. 93°. X-Ray data on neutral and acid salts are given. J. D. R.

Thermal decomposition of nickel and cobalt formates. F. CAUJOLLE (Compt. rend., 1939, 208, 445–447).— $(\text{HCO}_2)_2\text{Ni}\cdot 2\text{H}_2\text{O}$ when heated in vac. at 200–300° affords finely divided Ni, a mixture of gases containing CO_2 (62–85%), H_2 (25–08%), CO (11–37%), CH_4 (0–58%), and unidentified gas (0–12%), and some H_2O acid in reaction. Similarly, $(\text{HCO}_2)_2\text{Co}\cdot 2\text{H}_2\text{O}$ affords Co, CoO , and a mixture of gases containing CO_2 (39–97%), H_2 (27–60%), CO (31–48%), CH_4 (0–44%), and an unidentified gas (0–51%). Brochet's equation (cf. A., 1921, ii, 100) for the decomp. of the former does not account for the CO formed. The formation of CH_4 is probably due to a secondary reaction involving the finely divided metal.

J. L. D.

Identity of α - and β -linoleic acids. R. W. RIEMENSCHNEIDER, D. H. WHEELER, and C. E. SANDO (J. Biol. Chem., 1939, 127, 391–402).—The identity of α -, β -, and natural linoleic acid is proved by their physical properties and the similar yields of tetrabromostearic and sativic acids obtained from each. The stereochemical configurations are discussed.

R. S. C.

Cerebrosides. XVI. Cerebronic acid. E. KLENK and L. CLARENZ (Z. physiol. Chem., 1939, 257, 268–276; cf. Chibnall *et al.*, A., 1936, 454).—Synthetic α -hydroxy-*n*-tetracosanoic acid (I) [from erucic acid (II) by way of Et behenate, *n*-tetracosanoic and α -bromo-*n*-tetracosanoic acid] with AcCl yields α -acetoxy-*n*-tetracosanoic acid, m.p. 65.2–66.0°. Natural cerebronic acid (III) and synthetic (I) with excess of $0.1\text{N}\cdot\text{Pb}(\text{OAc})_4$ in AcOH give the aldehyde, $\text{C}_{22}\text{H}_{45}\cdot\text{CHO}$ [oxime, m.p. 98–99°, which with excess of Ac_2O gives the corresponding nitrile (IV), m.p. 52.0–52.5°]. Hydrolysis of (IV) gives tricosanoic acid, m.p. 77.7–78.1° (natural), 77.5–78.0° (synthetic), not identical in crystal spacing with tricosanoic acid, m.p. 78.5–79.0°, synthesised from (II). Fractional distillation of Me tricosanoate from natural (III) does not result in isolation of other acids although the fractions have different crystal spacings. Natural (III) is probably identical with (I).

W. McC.

Viscous acid, $\text{C}_{27}\text{H}_{52}\text{O}_3$, m.p. 97° (Na, m.p. 129–130°, and Pb, m.p. 138°, salts). Dihydroxy-acid, $\text{C}_{27}\text{H}_{54}\text{O}_5$, m.p. 127°. Viscosin, $\text{C}_{15}\text{H}_{26}\text{O}_2(\text{OH})_3\cdot\text{OMe}$, m.p. 294–295° (decomp.) (Pb and Ag salts; Ac_3 derivative, m.p. 222–223°).—See A., 1939, III, 342.

Condensation of α -keto-acids and amides. II. Pyruvic acid and acetamide. R. M. HERBST (J.

Amer. Chem. Soc., 1939, **61**, 483—486; cf. A., 1938, II, 397).—In the prep. of $(\text{NHAc})_2\text{CMe}\cdot\text{CO}_2\text{H}$ (I) from AcCO_2H (II) and NH_2Ac (Bergmann *et al.*, A., 1930, 585), a compound (III), $\text{OH}\cdot\text{CMe}(\text{NHAc})\cdot\text{CO}_2\text{H}\cdot 2\text{NH}_2\text{Ac}$, m.p. 115—116° (decomp.; corr.), is also formed. NH_2Ac and (II) in abs. EtOH also give (III). As judged by the mol. wt., (I) gives $\text{OH}\cdot\text{CMe}(\text{NHAc})\cdot\text{CO}_2\text{H} + 2\text{NH}_2\text{Ac}$ in cold, and (II) + $3\text{NH}_2\text{Ac}$ in hot, H_2O . With $\text{NHPh}\cdot\text{NH}_2$ (III) gives $\text{NHPh}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}_2\text{H}$ slowly in cold, but rapidly in hot, H_2O , and with 2 : 4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ in EtOH it gives the corresponding hydrazone only if first boiled for a few moments with HCl. Br does not react with (III). When heated at 100°/18—20 mm., (III) gives (I) and NH_2Ac , but at 76°/0.5 mm. it gives $\text{CH}_2\cdot\text{C}(\text{NHAc})\cdot\text{CO}_2\text{H}$ (IV) + $2\text{NH}_2\text{Ac}$. BzCl , AcCl , or PhNCO causes only dehydration. $\text{Ba}(\text{OH})_2$ and (III) give (II) and NH_2Ac . Analogous compounds containing other amides could not be prepared. Attempts to make (IV) the main reaction product from (II) and NH_2Ac failed. R. S. C.

Isomerisation of dimethyl maleate by hydrogen bromide and by hydrogen chloride. O. SUMAMURA (Bull. Chem. Soc. Japan, 1939, **14**, 22—28; cf. A., 1938, II, 48, 428).— Me_2 maleate and HCl or HBr, in absence of air, in the dark at room temp., afford Me_2 fumarate, the isomerisation being slower in CCl_4 . O_2 or pyrocatechol has no influence on the isomerisation. A mechanism of reaction is suggested. No isomerisation of isostilbene to stilbene occurs with HCl in presence of either reduced Ni or O_2 .

A. T. P.

Acryloxy-carboxylic acids and their esters.—See B., 1939, 242.

Michael condensation. V. Influence of the experimental conditions and the structure of the acceptor on the condensation. R. CONNOR and W. R. McCLELLAN (J. Org. Chem., 1939, **3**, 570—577).—*sec.* Amines (e.g., piperidine) are the safest catalysts in the Michael reaction since they seldom cause change other than the normal condensation. Where ring-closure, rearrangement, or formation of termol. compounds must be avoided amines give satisfactory results. They are less potent catalysts than Na alkoxides and with them the rate of reaction is rather slow even in favourable cases. NaOEt (one sixth to one third of an equiv.) may cause condensation in cases in which amines are ineffective. The condition is less drastic and less liable to cause side reactions than the use of 1 equiv. of NaOEt. The equiv. of catalyst is most likely to cause condensation and also side reactions. If a reactant or product undergoes alcoholysis readily in the presence of alkoxides or if the Na derivative of the active CH_2 compound is not readily formed, the Na derivative may be prepared by the use of Na or NaNH_2 . The solubility of the reactants is the chief desideratum in selecting a solvent: MeOH, EtOH, C_6H_6 , Et_2O , and dioxan have given satisfactory results. With Na alkoxides as catalysts the best results are obtained by keeping the mixture at room temp. for 20—150 hr. Higher temp. may give lower yields presumably because they favour retrogression and

increase the side reactions. However, if ring-closure or the formation of termol. compounds is desired, the reaction may be carried out under reflux. With *sec.* amines the change is so slow that long boiling is necessary. An arrangement of labilising groups in the order of their ability to activate the double linking of the acceptor cannot yet be given. In a system, $\text{CH}_2\cdot\text{CHL}_1$, the reactivity of the acceptor diminishes as the H atoms are replaced by larger groups; this is true whether substitution is at $\text{C}_{(\alpha)}$ or $\text{C}_{(\beta)}$. The reactivity of the acceptor is decreased if the substituent is alkyl, aryl, carbethoxy, or acyl. The magnitude of this effect probably depends largely on the size of the substituent, although in the case of negative groups such as $\cdot\text{CO}_2\text{R}$ or $\cdot\text{CN}$ the spatial effect may be modified by a polar effect which renders the system less unreactive than might be expected from the size of such groups. Groups which are not attached directly to the double linking of the acceptor have a greater influence on reactivity than is generally appreciated. The magnitude of their influence cannot be estimated but in predicting reactivity the possibility that remote groups may vastly alter the nature of the acceptor cannot be dismissed. The possibility of steric hindrance would suggest that the *o*-isomeride would be the least active of the nitro-cinnamic esters whereas actually the *p*-isomeride is the most turgid. Apparently steric influences by *o*-substituents are not extremely important—a fact confirmed by the reaction of benzylidenacetomesitylene. On the other hand, a *p*- NO_2 -group does not always prevent reaction. In the case of 6-bromocoumarin, substitution by Br causes a decrease in reactivity. The following compounds are new: β -hydroxy- β -phenyl- β -dicarbethoxymethylpropion-lactone, m.p. 52°, b.p. 203°/4 mm.; Et_2 α -phenyl- $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -dicarboxylate, b.p. 160—163°/6 mm.; Me α -*m*-nitrobenzylidenepropionate, m.p. 54—55°; Me_3 β -*m*-nitrophenylpropane- $\alpha\gamma\gamma$ -tricarboxylate, m.p. 97—98°, and the corresponding *o*-, m.p. 82—83°, and *p*-derivatives, m.p. 97—97.5°; Me_2 2 : 4 : 6-trimethylphenyl- β -phenylpropane- $\alpha\gamma$ -tricarboxylate, m.p. 82—83°. All m.p. are corr.

H. W.

Catalytic *cis-trans*-isomerisation and restricted rotation of diphenyl derivatives. W. I. GILBERT, J. TURKEVICH, and E. S. WALLIS (J. Org. Chem., 1939, **3**, 611—617).—Experiments on the influence of Na, AlCl_3 , FeCl_3 , ZnCl_2 , CrCl_3 , Fe_2O_3 , NiCl_2 , MgCl_2 , HgCl_2 , Hg_2Cl_2 , H_2O , and Fe_2O_3 on the isomerisation of Me_2 maleate to Me_2 fumarate show that there is no direct correlation between the magnetic character of the compound tested and its catalytic activity. Attempts are described to determine whether those experimental conditions which produce *cis-trans*-isomerism of the ethylenic double linking and those which temporarily destroy the double linking character would racemise an optically active diphenyl derivative. Et *d*-3 : 5-dinitro-6-1-naphthylbenzoate is not racemised by Pt-black, Na, or FeCl_3 and the acid is not racemised by exposure to sunlight in $\text{CHCl}_3\text{--CCl}_4$ or by Br in the same solvents. It is concluded that the existence of the double linking between the two Ph groups in Ph_2 derivatives cannot be detected by use of those

chemical agents which being about *cis-trans*-isomerisation. Therefore there may be no contribution of the type $\text{X}=\text{X}=\text{X}$ to the ordinary structure for Ph_2 or this contribution may be present but, due to the size of the substituents on the Ph groups, steric factors may come into play, and prevent the catalyst from affecting the coupling between these two π electrons either by distorting their orbits or by actual bond formation with the catalyst, and thus inhibit the formation of the necessary complex which of necessity on decomp. would give an equal no. of *d*- and *l*-forms. H. W.

Synthesis of cyclic derivatives of tartaric acid. V. TSUZUKI (Bull. Chem. Soc. Japan, 1939, 14, 19—22; cf. A., 1938, II, 60).— Et_2 *d*-tartrate and the respective ketone, with P_2O_5 , afford the following Et_2 alkylidenedioxy succinates of type $\text{CRR}'\text{O}-\text{CH}-\text{CO}_2\text{Et} : \text{R R}' =$ Me Et, b.p. $158^\circ/17$ mm., $[\alpha]_D^{20} -40.2^\circ$ in C_6H_6 , -36.0° in EtOH, -31.62° in cyclohexane, this order being followed with other analogues; Me Pr, b.p. $167.5^\circ/20$ mm., $[\alpha]_D^{20} -36.4^\circ$, -31.8° , -28.86° ; Et₂, b.p. $169^\circ/22$ mm., $[\alpha]_D^{20} -33.0^\circ$, -25.3° , -20.89° ; Me amyl, b.p. $180^\circ/15$ mm., $[\alpha]_D^{20} -31.13^\circ$, -27.33° , -24.19° ; Pr₂, b.p. $175^\circ/16$ mm., $[\alpha]_D^{20} -28.47^\circ$, -22.45° , -18.17° ; and Me nonyl, b.p. $218^\circ/15$ mm., $[\alpha]_D^{20} -26.03^\circ$, -21.38° , -18.93° . Me₂, b.p. $141^\circ/15$ mm., Pr₂, b.p. $167^\circ/15$ mm., and Pr₂ methylpropylidenedioxy succinate, b.p. $115-117^\circ/0.5$ mm., are prepared similarly. A. T. P.

Reduction of aconitic acid at the dropping mercury cathode. A. MIOLATI and G. SEMERANO (Z. Elektrochem., 1939, 45, 226—228).—The experiments of Siebert (cf. A., 1938, II, 471) are criticised, and views attributed by Siebert to the authors are corr. (see following abstract). C. R. H.

Reduction of aconitic acid at the dropping mercury cathode. H. SIEBERT (Z. Elektrochem., 1939, 45, 228).—A reply to Miolati and Semerano (see preceding abstract). C. R. H.

Micro-determination of ascorbic and dehydroascorbic acid.—See A., 1939, III, 290.

Formation of oxamide by oxidation of dehydroascorbic acid with hydrogen peroxide in ammoniacal solution. J. PARROD (Bull. Soc. chim., 1939, [v], 6, 392—396; cf. A., 1938, II, 307).—*l*-Ascorbic acid (I) loses 2 H with *p*-benzoquinone in $\text{Et}_2\text{O}-\text{H}_2\text{O}$ and the resulting solution (A) containing dehydroascorbic acid (II) decomposes slowly. A on oxidation by air in presence of NH_3 gives only a little $(\text{CO}\cdot\text{NH}_2)_2$ (III); with $\text{NH}_3-\text{H}_2\text{O}_2$ much more (III) is formed, which increases with amount of H_2O_2 , and then is approx. const. It is formed from (II). NH_3 reacts rapidly, previously to adding H_2O_2 ; when NH_3 and H_2O_2 are added to A simultaneously, the yield of (III) is \ll that obtained if H_2O_2 is added 2—60 sec. after the NH_3 . Freshly prepared A affords a max. yield of (III) comparable with that obtained from (I) by $\text{NH}_3 +$ air oxidation (*loc. cit.*). The amount of (III) formed decreases as A is kept, as does also the amount of (I) regenerated by H_2S . A. T. P.

Methyl ethers of araboascorbic acid and their isomerism. E. G. E. HAWKINS, E. L. HIRST, and J. K. N. JONES (J.C.S., 1939, 246—248).—*d*-Araboascorbic acid (I) in MeOH with CH_2N_2 in Et_2O yields 3-methyl-*d*-araboascorbic acid, m.p. 102° , $[\alpha]_D^{20} -26^\circ$ in H_2O , which on further methylation with CH_2N_2 yields 2:3-dimethyl-*d*-araboascorbic acid (a syrup), $[\alpha]_D^{20} -20^\circ$ in H_2O , -37° in MeOH, also formed from (I) with excess of CH_2N_2 , which with aq. $\text{Ba}(\text{OH})_2$ yields dimethyliso-*d*-araboascorbic acid (a syrup), $[\alpha]_D -5^\circ$ in H_2O , hydrolysed by MeOH-HCl containing 10% of H_2O to 2-methyl-*d*-araboascorbic acid, $[\alpha]_D -38^\circ$ in MeOH, -19° in H_2O . J. D. R.

Intermediary metabolism of citric acid.—See A., 1939, III, 301.

Reactions of humic acids with neutral salts. II. T. A. KUCHARENKO (Chim. Tverd. Topl., 1937, 8, 1064—1072).— $\text{Ca}(\text{OAc})_2$ reacts with humic acids liberating AcOH. The reaction may be used to determine CO_2H groups titrimetrically. The determination is quicker than the standard methylation method and can be used for humic substances with small or large CO_2H content. D. G.

Preparation and determination of glyoxal tetramethyl acetal. D. H. GRANGAARD and C. B. PURVES (J. Amer. Chem. Soc., 1939, 61, 428—429).— $[\text{CH}(\text{OMe})_2]_2$ (prep. from glyoxal disulphate described), b.p. $98-100^\circ/110$ mm., is quantitatively converted by 2N-HCl into $(\text{CHO})_2$ (determined as dinitrophenylhydrazone or by Ariyama's method). Separation of the acetal from solvents is described. R. S. C.

Action of acid chlorides on aliphatic ethylenic hydrocarbons in presence of stannic chloride. I, II. J. COLONGE and K. MOSTAFAVI (Bull. Soc. chim., 1939, [v], 6, 335—342, 342—354).— $\text{CMe}_2\text{:CHMe}$ and EtCOCl , with SnCl_4 as catalyst, followed by hydrolysis (HCl), afford CMe_2EtCl , ϵ -chloro- $\delta\epsilon$ -dimethylhexan- γ -one (I), b.p. $74-78^\circ/17$ mm., and $\delta\epsilon$ -dimethyl- Δ^5 - (53% of total unsaturated ketone), b.p. $164-166^\circ/750$ mm. [semicarbazone, m.p. 209° ; (?) 1-carbamyl-4:5:5-trimethyl-3-ethyl-2-pyrazoline, m.p. 130°], and Δ^4 -hexen- γ -one (47%), b.p. $158-162^\circ/750$ mm. (semicarbazone, m.p. $108-110^\circ$). The mixed unsaturated ketones (II) are obtained from (I) by refluxing with NPhMe_2 , and are purified by hydrolysing their semicarbazones with $\text{H}_2\text{C}_2\text{O}_4$; the α - tends to isomerise to the β -unsaturated ketone during such hydrolysis. Both ketones are hydrogenated (Pt-black) to $\delta\epsilon$ -dimethylhexan- γ -one, b.p. $151-153^\circ/730$ mm. (semicarbazone, m.p. 98°). The yield of (II) is 60% with SnCl_4 , and 40, 16, 13, and 0% with TiCl_4 , ZnCl_2 , AlCl_3 , and HgCl_2 , respectively. $\text{CMe}_2\text{:CHMe}$, AcCl , and SnCl_4 afford δ -chloro- $\gamma\delta$ -dimethylpentan- β -one, b.p. $60-64^\circ/14$ mm., converted by NPhMe_2 into mixed unsaturated ketones, separated (as above) into $\gamma\delta$ -dimethyl- Δ^7 - (III) (80%), b.p. $146-147^\circ$ (semicarbazone, m.p. $199-200^\circ$), and Δ^5 -penten- β -one (20%), b.p. $140-144^\circ$ (semicarbazone, m.p. $112-114^\circ$), the constitutions of the semicarbazones being supported by the application of tests described by Dœuvre (A., 1936, 587) for terminal

CMe_2 and CH_2 . (III) and NaOBr afford $\alpha\beta$ -trimethylacrylic acid. Hydrogenation (Pt-black) of the mixed ketones gives solely $\gamma\delta$ -dimethylpentan- β -one, b.p. $136\text{--}138^\circ/760$ mm. (semicarbazone, m.p. 113°). Pr^iCOCl similarly affords ϵ -chloro- $\beta\delta\epsilon$ -trimethylhexan- γ -one, b.p. $74\text{--}79^\circ/14$ mm., converted into $\beta\delta\epsilon$ -trimethyl- Δ^8 (semicarbazone, m.p. 190° ; sublimes at 188°) and Δ^4 -hexen- γ -one (semicarbazone, m.p. $110\text{--}111^\circ$), which give $\beta\delta\epsilon$ -trimethylhexan- γ -one, b.p. $162\text{--}166^\circ/760$ mm. Bu^iCOCl and CMe_2CHMe also yield mixed unsaturated ketones, hydrogenated to $\beta\beta\delta\epsilon$ -tetramethylhexan- γ -one, b.p. $172\text{--}175^\circ/760$ mm. With compounds $\text{CRR}'\text{CHR}'$, the Cl of $\text{R}\cdot\text{COCl}$ attaches itself to the more substituted C. β -Methylpropene and EtCOCl yield, through the chloroketone, ϵ -methyl- Δ^8 -hexen- γ -one, b.p. $147\text{--}148^\circ/760$ mm. (semicarbazone, m.p. 163°), solely. $(\text{CMe}_2)_2$, AcCl , and SnCl_4 afford $\text{CMe}_2\text{Pr}^i\text{Cl}$, δ -chloro- $\gamma\gamma\delta$ -trimethylpentan- β -one, m.p. 82° , b.p. $90^\circ/30$ mm., and thence $\gamma\gamma\delta$ -trimethyl- Δ^8 -penten- β -one, b.p. $151^\circ/753$ mm. [ozonolysis of its semicarbazone, m.p. 152° (157°), indicates a terminal CH_2], hydrogenated to $\gamma\gamma\delta$ -trimethylpentan- β -one, b.p. $152\text{--}154^\circ/753$ mm. (semicarbazone, m.p. 150°) (cf. Whitmore *et al.*, A., 1933, 1140). β -Methyl- Δ^8 -hexene and AcCl similarly afford mixed unsaturated ketones, hydrogenated to γ -isopropylhexan- β -one, b.p. $172\text{--}173^\circ/744$ mm. (semicarbazone, m.p. $129\text{--}130^\circ$). Δ^4 -Heptene reacts with AcCl , but no unsaturated ketone was obtained. $(\text{CHCl})_2$ and $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Cl}$ do not react with AcCl .

A. T. P.

Transformation of carboxylic acids into ketones by means of their lead salts. J. KENNER and F. MORTON (Ber., 1939, 72, [B], 452–456).—Reasons are advanced for considering the Pb salts of acids particularly suitable for the prep. of ketones. The salts of the higher fatty acids, of unsaturated acids, and of the H esters of the higher dicarboxylic acids lose CO_2 smoothly at $240\text{--}310^\circ$ until about $50\text{--}70\%$ of the theoretically possible CO_2 has been evolved. The liquid then solidifies to an intermediate product from which ketone cannot be isolated immediately. If derived from a fatty acid it gives an excellent yield of ketone when distilled. Salts of unsaturated acids give a black resinous product which gives only a little ketone when distilled under diminished pressure and is very slowly attacked by $(\text{NH}_4)_2\text{S}$. HCO_2H transforms it into a mixture of ketone and unchanged acid. The method is also applicable to salts of H esters. The method has been applied to the salts of AcOH , EtCO_2H , $\text{Pr}^i\text{CO}_2\text{H}$, $\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$, $\text{C}_7\text{H}_{13}\cdot\text{CO}_2\text{H}$, $\text{C}_8\text{H}_{15}\cdot\text{CO}_2\text{H}$, $\text{C}_{10}\text{H}_{21}\cdot\text{CO}_2\text{H}$, lauric and stearic acid, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{C}_3\text{H}_5\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{C}_4\text{H}_9\text{Ph}\cdot\text{CO}_2\text{H}$, undecenoic, chaulmoogric, and hydnicaric acid, *Me H suberate*, b.p. $185\text{--}186^\circ/18$ mm., m.p. $14\text{--}15^\circ$, *Me H azelaate*, *Me H* and *Et H* sebacate. The following are new: *chaulmoogrone*, $\text{C}_{35}\text{H}_{69}\text{O}$, m.p. $59\cdot5^\circ$; *hydnicarpone*, m.p. 52° ; α -*diphenylheptan-8-one*, b.p. $186\text{--}187^\circ/0\cdot8$ mm.; α -*diphenylnonan-8-one*, b.p. $205\text{--}207^\circ/0\cdot5$ mm. (oxime, m.p. 43°); *Me*, θ -*ketopentadecan- $\alpha\alpha$ -dicarboxylate*, b.p. $242\text{--}244^\circ/15$ mm., m.p. 42° (free acid, m.p. 114°); α -*ketononadecanone- α -dicarboxylic acid*, m.p. 124° ; *Me H pimelate*, b.p. $168\text{--}169^\circ/17$ mm., m.p. 5° .

H. W.

Symmetrical dialkoxyacetones. H. R. HENZE and B. G. ROGERS (J. Amer. Chem. Soc., 1939, 61, 433–435).— $\text{CO}(\text{CH}_2\cdot\text{OR})_2$ ($\text{R} = \text{Alk}$) could not be obtained from $\text{CO}(\text{CH}_2\text{Cl})_2$ and NaOAlk , but are prepared from $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ and NaOAlk , followed by $\text{Na}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ at $15\text{--}20^\circ$. $\text{OR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (prep. from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$) gives $(\text{OR}\cdot\text{CH}_2\cdot\text{CO})_2\text{CH}\cdot\text{CO}_2\text{Et}$ and thence by aq. K_2CO_3 only 10% of $\text{CO}(\text{CH}_2\cdot\text{OR})_2$. The following are described. *n*-Amyl chloroacetate, b.p. $198\text{--}199^\circ/744$ mm.; *Bu*ⁿ *n*-butoxy, b.p. $123\text{--}123\cdot5^\circ/30$ mm., and *n*-amyl *n*-amyl-oxy-acetate, b.p. $148\text{--}149^\circ/35$ mm.; *glycerol* α -*Me*, b.p. $65\cdot5\text{--}66^\circ/9$ mm., *Et*, b.p. $61\cdot5\text{--}62^\circ/2$ mm., Pr^i , b.p. $82\text{--}83^\circ/2$ mm., Pr^n , b.p. $74\text{--}75^\circ/2$ mm., *Bu*ⁿ, b.p. $104\text{--}105^\circ/2$ mm., *Bu*^t, b.p. $105\text{--}105\cdot5^\circ/4$ mm., *sec*-*Bu*, b.p. $95\text{--}96^\circ/2$ mm., *diisooamyl*, b.p. $125\text{--}126^\circ/2$ mm., and *di-n*-amyl, b.p. $124\text{--}125^\circ/2$ mm., ether; *s*-dimethoxy, b.p. $78\text{--}78\cdot5^\circ$ (2 : 4-dinitrophenylhydrazones, m.p. $119\cdot5\text{--}120\cdot5^\circ$), *diethoxy*, b.p. $105\text{--}105\cdot5^\circ/35$ mm. (semicarbazone, m.p. $90\text{--}91^\circ$), *di-n*, b.p. $124\text{--}125^\circ/28$ mm. (semicarbazone, m.p. $85\cdot5\text{--}87^\circ$), and *diiso-propoxy*, b.p. $75\text{--}76\cdot5^\circ/1$ mm., *di-n*, b.p. $111\cdot5\text{--}112\cdot5^\circ/3$ mm. (semicarbazone, m.p. $82\cdot5\text{--}83\cdot5^\circ$), *diiso*, b.p. $91\text{--}93^\circ/1$ mm., and *di-sec-butoxy*, b.p. $88\text{--}90\cdot5^\circ/1$ mm., *di-n*, b.p. $128\text{--}129\cdot5^\circ/1$ mm., and *diiso-amyl-oxy*, b.p. $120\text{--}122^\circ/1$ mm., *acetone*. *d*, *n*, γ , and *parachors* are given. Temp. are corr.

R. S. C.

Synthesis from thujaketone of some new hydroterpenoids. J. WERNER and M. T. BOGERT (J. Org. Chem., 1939, 3, 578–587).—*d*-Thujone, obtained from thuja-leaf oil (tribromide, m.p. $121\text{--}122^\circ$; 2 : 4-dinitrophenylhydrazones, m.p. $106\text{--}107^\circ$), is converted by (modified) oxidation with aq. KMnO_4 into α -thujaketonic acid, m.p. $74\text{--}75^\circ$ (oxime, m.p. $175\text{--}176^\circ$), decarboxylated at $275\text{--}325^\circ$ to thujaketone [β -methyl- γ -methyleneheptan- β -one] (I), b.p. $183\text{--}188^\circ$ (semicarbazone, m.p. $141\text{--}142^\circ$; 2 : 4-dinitrophenylhydrazones, m.p. $73\text{--}74^\circ$). $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn convert (I) in $\text{C}_6\text{H}_6\text{--PhMe}$ into *Me* β -hydroxy- $\beta\zeta$ -dimethyl- ϵ -methyleneoctoate, b.p. $113\text{--}114^\circ/3$ mm. The corresponding acid (II), b.p. $144\text{--}146^\circ/3$ mm., is hydrogenated (Pd-C in 80% MeOH) to β -hydroxy- $\beta\zeta$ -trimethyl-octoic acid, b.p. $164\text{--}166^\circ/6$ mm. Dehydration of (II) by P_2O_5 in boiling C_6H_6 affords $\beta\zeta$ -dimethyl- ϵ -methylene- Δ^8 -octenoic acid (III), b.p. $127\text{--}128^\circ/2$ mm. Slow distillation transforms (II) into $\beta\zeta$ -dimethyl- δ -methylene- Δ^8 -heptene, b.p. $158\text{--}159^\circ$, also obtained in poorer yield from (III) and oxidised by KMnO_4 to β -methylheptano- $\gamma\zeta$ -dione in small amount. Gradual addition of (I) to well-cooled PCl_5 gives β -chloro- ζ -methyl- ϵ -methylene- Δ^8 -heptene, b.p. $95\text{--}96^\circ/18$ mm., oxidised to COMePr^i in small yield. Methylheptenone (IV) is transformed by the successive action of NaHSO_3 and KCN into α -hydroxy- $\alpha\epsilon$ -dimethyl- Δ^8 -heptenonitrile, b.p. $115\text{--}117^\circ/2$ mm. Analogously, (I) affords α -hydroxy- $\alpha\epsilon$ -dimethyl- δ -methylenheptenonitrile, b.p. $116\text{--}118^\circ/2$ mm. The following alcohols are synthesised by the standard Grignard reaction either from (I) or Bu^iCHO or by reduction of the corresponding unsaturated alcohol: $\beta\zeta$ -dimethyl- γ -methyleneheptan- β -ol, b.p. $97\text{--}99^\circ/19$ mm.; $\beta\zeta$ -dimethyl- γ -methylenedodecan- ζ -ol, b.p. $150\text{--}153^\circ/15$ mm.; β -cyclohexyl- ζ -methyl- ϵ -methylene-

heptan- β -ol, b.p. 122—124°/3 mm.; β - ζ -dimethyl- γ -methylene- η -isobutyltridecan- ζ -ol, b.p. 157—157.5°/2 mm.; β - γ -trimethyltridecan- ζ -ol, b.p. 149—151°/17 mm.; β -methyldecan- δ -ol, b.p. 123—125°/12 mm. δ -Bromo- β -methyldecan has b.p. 115—118°/17 mm. Et α -cyano- β - ζ -dimethyl- $\Delta^{\alpha\alpha}$ -octadienoate, b.p. 151—152°/12 mm., is obtained from (IV), $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and NH_2Ac in $\text{AcOH}\cdot\text{Ac}_2\text{O}$. The odours of these compounds differ from and are more pleasant than those of the analogously constituted compounds obtained from (IV). In the case of the *tert.* alcohols synthesised by the Grignard reaction, the agreeableness of the odour diminishes with increase in the mol. wt. of the hydrocarbon introduced. All m.p. are corr.

H. W.

Degradation reaction in organic chemistry. A. SCHÖNBERG (Nature, 1939, 143, 113).—A correction (cf. A., 1939, II, 49).

L. S. T.

Acetylation of carbohydrates by keten. C. D. HURD, S. M. CANTOR, and A. S. ROE (J. Amer. Chem. Soc., 1939, 61, 426—428).—Anhyd. glucose, keten, and a drop of H_2SO_4 in COMe_2 give a glass containing 4.59 Ac; p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ does not catalyse acetylation in dioxan; in $\text{C}_5\text{H}_5\text{N}$ (no acid) an impure, glassy triacetate, $[\alpha]_D^{20} + 39.5^\circ$ in CHCl_3 (converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ into a glass, $[\alpha]_D + 48.8^\circ$ in CHCl_3), is produced with a small amount of the compound, m.p. 204° (Wollenberg, A., 1934, 1336), formed with dehydroacetic acid (I) from $\text{C}_5\text{H}_5\text{N}$. In dioxan or with a drop of H_2SO_4 in AcOH an oily triacetate, converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ into the α -tetra-acetate, is obtained. 6-Triphenylmethyl- α -methylglucoside with $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ gives only, and with keten in Ac_2O gives mainly, the 1 : 2 : 4-triacetate, m.p. 136°, and 1 : 2-isopropylideneglucose gives by either method the triacetate. $\text{CO}\cdot\text{CHAc}$ with $\text{C}_5\text{H}_5\text{N}$ -dioxan gives (I), which is unchanged by this reagent.

R. S. C.

Oxidation of aldoses by hypoiodite. I. K. MYRBÄCK (Svensk Kem. Tidskr., 1939, 51, 7—11).—Errors in the determination of aldoses by NaOI are discussed, and the importance of keeping $[\text{NaOH}]$ low is stressed.

M. H. M. A.

Isolation of derivatives of 2-methylglucose and 3-methylglucose from a partly methylated cellulose. W. J. HEDDLE and E. G. V. PERCIVAL (J.C.S., 1939, 249—250).—Cellulose (surgical cotton) methylated by the method of Piwonka (A., 1936, 1235) yields a partly methylated cellulose from which, by hydrolysis with 1% $\text{HCl}\cdot\text{MeOH}$, 2- and 3-methylglucose are isolated as the phenylhydrazones and osazone respectively.

J. D. R.

Isolation of an anhydro-sugar from agar. E. G. V. PERCIVAL, J. C. SOMERVILLE, and I. A. FORBES (Nature, 1938, 142, 797—798).—Hydrolysis of methylated agar with $\text{HCl}\cdot\text{MeOH}$ affords 2 : 4 : 6-trimethylmethylgalactoside and a non-homogeneous syrup from which a cryst. dimethylanhydromethylhexoside (X), $\text{C}_6\text{H}_{10}\text{O}_2(\text{OMe})_3$, b.p. 85—90°/0.05 mm., m.p. 81°, $[\alpha]_D^{20} + 75^\circ$ in H_2O , $+ 85^\circ$ in CHCl_3 , is isolated. This gives a strong Selivanov test and is converted by $\text{N}\cdot\text{H}_2\text{SO}_4$ in 24 hr. into the anhydrosugar (I), $[\alpha]_D^{17} - 23^\circ$. Direct methylation of 3 : 6-anhydro- α -

methylgalactoside gives 2 : 4-dimethyl-3 : 6-anhydro- α -methylgalactoside, b.p. 90°/0.05 mm., $[\alpha]_D^{20} + 87^\circ$ in CHCl_3 , which gives the Selivanov reaction and is hydrolysed by $\text{N}\cdot\text{H}_2\text{SO}_4$ in 24 hr. to 2 : 4-dimethyl-3 : 6-anhydro-d-galactose (II), $[\alpha]_D^{20} + 22^\circ$. It is probable that (I) and (II) are optical antipodes.

H. W.

3 : 6-Anhydro-l-galactose in agar. E. G. V. PERCIVAL and I. A. FORBES (Nature, 1938, 142, 1076).—The substance, X, derived from agar (preceding abstract) is shown to be 2 : 4-dimethyl-3 : 6-anhydro- β -methyl-l-galactoside (cf. A., 1939, II, 50). 3 : 6-Anhydro- β -methyl-d-galactoside (I), m.p. 118°, $[\alpha]_D^{20} - 113^\circ$ in H_2O , has been synthesised from l-bromo- α -d-galactose triacetate 6-*p*-toluenesulphonate by treatment with $\text{Ag}_2\text{CO}_3 + \text{MeOH}$, and deacylation (NaOH). Methylation of (I) gives a quant. yield of 2 : 4-dimethyl-3 : 6-anhydro- β -methyl-d-galactoside, m.p. 82°, $[\alpha]_D^{20} - 77^\circ$ in H_2O , $- 86^\circ$ in CHCl_3 , which is shown to be the enantiomorph of X.

L. S. T.

Crystalline β -methylmannofuranoside and mannose dimethyl acetal. E. PACSU and A. SCATTERGOOD (J. Amer. Chem. Soc., 1939, 61, 534—536).—d-Mannose Et_2 mercaptal (I) yields 60% of α - and β -methylmannofuranoside, m.p. 47°, $[\alpha]_D^{20} - 107^\circ$ in H_2O , the latter product being isolated as a compound, $\text{X}\cdot\text{CaCl}_2\cdot 3\text{H}_2\text{O}$, $[\alpha]_D^{20} - 58^\circ$ in H_2O , which is also obtained from the syrupy reaction product of mannose and $\text{HCl}\cdot\text{MeOH}$. The penta-acetate of (I) yields d-mannose Me_2 acetal, m.p. 101°, $[\alpha]_D^{20} + 0.6^\circ$ in H_2O .

R. S. C.

Reaction for distinction of fructose from glucose. O. M. TSCHERNITSOV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 583—584).—The reaction suggested by Zmachinski (A., 1938, II, 172) is not sp. for fructose but proceeds readily with glucose and other aldoses, and only slightly more slowly with disaccharides.

J. D. R.

Structure of γ -sugars. I. Parachors of partly and fully methylated derivatives of γ -fructose. F. HARTLEY and W. H. LINNELL (Quart. J. Pharm., 1938, 11, 714—721).—The vals. of $[P]$ of furfuraldehyde and piperonal (305.9—307.1 for the latter) confirm that no anomaly occurs in the val. of $[P]$ due to the presence of O in 5-membered rings. The vals. of $[P]$ for sucrose, fructose, and glucose (in aq. solution) are anomalous and irregular, whilst those for tetramethyl- γ -fructose and γ -methylfructoside differ significantly from the vals. calc. for either the furanose or the propylene oxide structure.

F. O. H.

Ketoses. II. Structure of α -d-tagatose. (MME.) Y. KHOUVINE, G. ARRAGON, and Y. TOMODA (Bull. Soc. chim., 1939, [v], 6, 354—359; cf. A., 1938, II, 473).— α -d-Tagatose (I), m.p. 162° (cf. Danilow *et al.*, A., 1930, 1411; Reichstein *et al.*, A., 1934, 872), when redistilled with dry $\text{C}_5\text{H}_5\text{N}$ and Ac_2O at 0—2° (4 hr.) gives α -d-tagatose penta-acetate, m.p. 132°, $[\alpha]_D^{20} + 30.2^\circ$ in CHCl_3 , $- 52.0^\circ$ in MeOH (Raman spectrum shows no band at 2800 Å.); Ac_2O with ZnCl_2 affords a syrup. (I) and $\text{HCl}\cdot\text{MeOH}$ at 28° give α -d-methyltagatoside (II), m.p. 128°, $[\alpha]_D^{20} + 56.8^\circ$ in MeOH , $+ 47.8^\circ$ in H_2O ; acid hydrolysis gives (I), with mutarotation. (II) and

$\text{Ac}_2\text{O}-\text{C}_6\text{H}_5\text{N}$ at 0° , then at room temp., give the Ac_4 derivative, m.p. 125° , $[\alpha]_{\text{D}}^{25} +43.8^\circ$ in C_6H_6 , $+23.8^\circ$ in CHCl_3 , and $+6.2^\circ$ in MeOH . (II) in MeOH with $\text{MeI}-\text{Ag}_2\text{O}$ (8 to 10 successive methylations) gives *tetramethyl- α -D-methyltagatoside* (III), b.p. $40^\circ/0.001$ mm., $[\alpha]_{\text{D}}^{20} +21.4^\circ$ in MeOH (Raman spectra do not indicate CO), oxidised by HNO_3 (d 1.49) to *l*-dimethoxysuccinic and *d*-arabotrimethoxyglutaric acids. (II) and $\text{Me}_2\text{SO}_4-\text{NaOH}-\text{CCl}_4$ at $60-65^\circ$ afford syrups, $[\alpha]_{\text{D}}^{20} +28.7^\circ$ and $+30.8^\circ$, respectively, in MeOH . (I) and aq. $\text{NaOH}-\text{Me}_2\text{SO}_4$ at $60-70^\circ$ give *tetramethyl- β -D-methyltagatoside*, $[\alpha]_{\text{D}}^{20} +9.7^\circ$ in MeOH , in poor yield. Hydrolysis of (III) with aq. HCl gives *tetramethyl- α -D-tagatose*, b.p. $55^\circ/0.0001$ mm., $[\alpha]_{\text{D}}^{20} -3.4^\circ$ in MeOH . (I) (and its derivatives) has a pyran configuration, more stable than those of β -D-fructose and α -L-sorbose.

A. T. P.

Structure and configuration of perseulose (L-galaheptulose). R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 336-340).—Perseulose (I) (prep. from perseitol in 91.6% yield by *Acetobacter suboxydans*), $+0.5\text{H}_2\text{O}$, m.p. $102-103^\circ$ (corr.), $[\alpha]_{\text{D}}$ about $-102^\circ \rightarrow -86^\circ$ (anhyd.), is shown to be *L*-galaheptulose. The phenylosazone, decomp. $240^\circ \pm 1^\circ$ (block), $[\alpha] -114^\circ \rightarrow -35^\circ$ in $\text{C}_6\text{H}_5\text{N}$, and the *penta-acetate*, m.p. $117-118^\circ$ (corr.), $[\alpha] -86.8^\circ$ in CHCl_3 , thereof are enantiomorphs of the derivatives of *D*-galaheptulose. *dl*-Galaheptosephenylosazone, m.p. 222° (corr.; capillary), 259° (block), and its *penta-acetate*, m.p. $125-126^\circ$ (shrinks at $116-117^\circ$), are described. Raney $\text{Ni}-\text{H}_2$ at $100^\circ/167$ atm. reduces (I) in H_2O to *D*-gulo-*L*-gala- and *L*-gala-*D*-gluco-heptitol, m.p. 141° , $[\alpha] -2.4^\circ$ in H_2O [*hepta-acetate*, m.p. 118° (corr.), $[\alpha] -11.4^\circ$ in CHCl_3 ; enantiomeride obtained by similar reduction of *D*-gala-*L*-glucoheptose]. *dl*-Galaglucoheptitol, m.p. 138° (corr.), and its *hepta-acetate*, m.p. 127° (corr.), are also described.

R. S. C.

Oxidative degradation of perseulose to L-galactonic acid. N. K. RICHTMYER, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 340-343).— O_3 converts perseulose (I) in N-KOH at $23-27^\circ$ in 46% yield into *K* *L*-galactonate, $+\text{H}_2\text{O}$, $[\alpha] -2.95^\circ$ in H_2O , $+12.2^\circ \rightarrow +61.2^\circ$ in N-HCl , which yields the *Pb* salt, $[\alpha] +13.6^\circ$ in H_2O , $+14.8^\circ \rightarrow +61.2^\circ$ in N-HNO_3 , and thence (H_2S) γ -*L*-galactonolactone, sinters at $\sim 128^\circ$, m.p. 134° , $[\alpha] +78.4^\circ$ in H_2O . The *D*-salts mutarotate similarly. This confirms the structure of (I).

R. S. C.

Oxidative degradation of sedoheptulose to D-altronic acid. N. K. RICHTMYER, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 343-345).—Crude sedoheptulose (prep. from *Sedum spectabile*) in N-KOH is converted by O_2 etc. into *Ca* *D*-altronate, $+3.5\text{H}_2\text{O}$, $[\alpha]_{\text{D}}^{20} +11.5^\circ \rightarrow +24.8^\circ$ in N-HCl , and is thus *D*-alatroheptulose (cf. Ettel, A., 1933, 47).

R. S. C.

Polysaccharides synthesised by micro-organisms. IV. Molecular constitution of luteose. C. G. ANDERSON, W. N. HAWORTH, H. RAISTRICK, and M. STACEY (Biochem. J., 1939, 33, 272-279).—Elimination of the malonyl residues from luteic acid, one of the metabolic products of *Penicillium luteum*,

Zukal, gives rise to a polysaccharide, *luteose*; this consists of a closed chain type of mol. mainly composed of glucopyranose units linked through the 1:6-positions, as indicated by the isolation of 2:3:4-trimethylglucose in 85% yield from methylated luteose, together with 10% of dimethylglucose.

P. G. M.

Cæsioside, $\text{C}_{26}\text{H}_{28}\text{O}_{15} \cdot 3\text{H}_2\text{O}$, m.p. $225-230^\circ$, $[\alpha]_{\text{D}}^{20} -220^\circ$ in 0.1N- NaOH .—See A., 1939, III, 343.

Partial oxidation of starch by bromine. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1939, 15, 107-108).—Oxidation of starch paste in presence of CaCO_3 by Br at room temp. produces *uronodextrin*, $[\alpha]_{\text{D}}^{25} +181.72^\circ$ in H_2O (acetate, m.p. 145°). It is sol. in H_2O and pptd. by EtOH , Ca(OH)_2 , and Ba(OH)_2 , but not by CuSO_4 . It is scarcely affected by taka-diastase.

J. N. A.

Constitution and enzymic degradation of starch. K. MYRBÄCK (Suomen Kem., 1939, 12, A, 19-29).—A review. M. H. M. A.

Recent results in the study of starch. II. M. SAMEC and M. BLINC (Kolloid-Beih., 1939, 49, 75-314; cf. A., 1938, II, 262).—A review of work on the degradation of starch by enzymes and acids.

F. L. U.

[Preparation of] sec. amines by the Leuckart synthesis. A. NOVELLI (J. Amer. Chem. Soc., 1939, 61, 520-521).— HCO-NHR and the appropriate ketone at $190-230^\circ$ give 50-80% yields of the *hydrochlorides*, $\text{NHR}'\text{HCl}$, in which (a) $\text{R} = \text{CHPhMe}$, $\text{R}' = \text{Me}$, m.p. $178-179^\circ$ (lit. 173°), *Et*, m.p. $199-200^\circ$ (lit. 201°), and *Bu*, m.p. $154-155^\circ$, (b) $\text{R} = \text{p-C}_6\text{H}_4\text{MeCHMe}$, $\text{R}' = \text{Me}$, m.p. $159-160^\circ$, *Et*, m.p. $217-218^\circ$, and *Bu*, m.p. $159-160^\circ$, (c) $\text{R} = \text{p-C}_6\text{H}_4\text{Cl-CHMe}$, $\text{R}' = \text{Me}$, m.p. $199-200^\circ$, *Et*, m.p. $<250^\circ$, and *Bu*, m.p. $174-175^\circ$, and (d) $\text{R} = \text{p-C}_6\text{H}_4\text{Br-CHMe}$, $\text{R}' = \text{Me}$, m.p. $196-197^\circ$, *Et*, m.p. $<250^\circ$, and *Bu*, m.p. $174-175^\circ$.

R. S. C.

Protein metabolism. IV. Stability of nitrogen in organic compounds. A. S. KESTON, D. RITTENBERG, and R. SCHOENHEIMER (J. Biol. Chem., 1939, 127, 315-318).—When two N-containing components, one of which contained "labelled" N, were heated at 100° in aq. solution, no exchange of the N could be detected in the following systems: (a) NH_2 -acid (I)- NH_3 ; (b) (I)-(I); (c) hippuric acid-(I); (d) $\text{CO(NH}_2)_2$ -(II)-(I). Some exchange may occur between (II) and NH_3 in H_2O at 105° but in any case the reaction is a slow one. The guanidogroup in arginine does not exchange N under the conditions investigated.

W. O. K.

Effect of pyrrole on the oxidation of amines and the non-natural isomerides of certain amino-acids.—See A., 1939, III, 78.

Isolation of spermine as flavianate. H. FUCHS (Z. physiol. Chem., 1939, 257, 149-150).—Spermine (I) salts yield with excess of flavianic acid (II) *spermine tetraflavianate*, decomposed by H_2O at 100° with production of the *disflavianate* (III), chars $290-300^\circ$. (III) is readily converted into the pure tetra-pyricate and free base. With CuCO_3 at 100° (I) yields a deep lilac colour whilst putrescine yields

almost no colour and spermidine (IV) only a faint blue colour. The phosphate of (IV) gives with (II) the *triflavanate*, decomp. with frothing 249–250°.

W. McC.

Complex phosphododecamolybdates.—See A., 1939, I, 212.

Phosphomolybdates of ethanolamines; triethanolamine phosphotungstate. A. TETTAMANZI (Atti R. Accad. Sci. Torino, 1935, 71, I, 116–124; Chem. Zentr., 1937, i, 554).—The following sparingly sol. yellow cryst. compounds have been prepared: $[\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{OH}]_5\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 2\text{HNO}_3\cdot 10\text{H}_2\text{O}$; $[\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{OH}]_5\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 1\cdot 5\text{HNO}_3$; $[\text{NH}(\text{C}_2\text{H}_4\cdot\text{OH})_2]_4\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot \text{HNO}_3$; $[\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3]_4\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 2\text{HNO}_3$; $[\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3]_5\cdot\text{H}_7[\text{P}(\text{Mo}_2\text{O}_7)_6]\cdot 1\cdot 5\text{HNO}_3\cdot 5\text{H}_2\text{O}$; $[\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3]_3\cdot\text{H}_7[\text{P}(\text{W}_2\text{O}_7)_6]$ (bluish-white).

A. J. E. W.

Configuration of glucosamine (chitosamine). W. N. HAWORTH, W. H. G. LAKE, and S. PEAT (J.C.S., 1939, 271–274).—4 : 6-Dimethyl-2 : 3-anhydro- β -methylmannoside when heated at 130° for 30 hr. with $\text{MeOH}\cdot\text{NH}_3$ yields a *dimethylmethylhexosaminide* (I), b.p. 125°/0.02 mm., $[\alpha]_D^{25} -103^\circ$ in MeOH [*diacetate* (II), b.p. 185°/0.004 mm.]. With Ac_2O in MeOH at room temp. (I) yields a mixture, b.p. 184° (bath)/0.005 mm., of 3-acetamido-4 : 6-dimethyl- β -methyl-d-altropyranoside (III), m.p. 150°, $[\alpha]_D^{25} -108.0^\circ$ in MeOH , and 2-acetamido-4 : 6-dimethyl- β -methyl-d-glucopyranoside (IV), m.p. 187°, $[\alpha]_D^{25} -21.5^\circ$ in MeOH , both of which are formed from (II) with Na in EtOH . Methylation of (III) with $\text{MeI}\cdot\text{Ag}_2\text{O}$ yields 3-acetamido-2 : 4 : 6-trimethyl- β -methylaltroside (V), b.p. 160° (bath)/0.01 mm., m.p. 116°, $[\alpha]_D^{25} -97.7^\circ$ in CHCl_3 , -87.0° in H_2O , -83.0° in MeOH , whilst (IV) similarly treated yields 2-acetamido-3 : 4 : 6-trimethyl- β -methyl-d-glucopyranoside, m.p. 195–196°, identical with the *N*-acetyltrimethyl- β -glucosaminide prepared by Cutler *et al.* (A., 1938, II, 46) from natural glucosamine, which is therefore related to the parent sugar glucose. Methyl-*epi*-glucosamine hydrochloride with $\text{MeOH}\cdot\text{Ac}_2\text{O}\cdot\text{AgOAc}$ gives 3-acetamido- β -methylaltroside, which on methylation ($\text{MeI}\cdot\text{Ag}_2\text{O}$) yields (V).

J. D. R.

Derivatives of methylated glucosamine. W. O. CUTLER and S. PEAT (J.C.S., 1939, 274–279).—Triacetyl- β -methylglucosaminide hydrobromide with BzCl in aq. NaOH yields *tetrabenzoyl- β -methylglucosaminide*, m.p. 182°, $[\alpha]_D^{25} +18.7^\circ$ in CHCl_3 , whilst with BzCl and Ag_2CO_3 in H_2O *N*-benzoyltriacetyl- β -methylglucosaminide, m.p. 222°, $[\alpha]_D^{25} +29.6^\circ$ in CHCl_3 , is formed, methylated (Me_2SO_4 in COMe_2 -aq. NaOH) to *N*-benzoyltrimethyl- β -methylglucosaminide (I), m.p. 198°, $[\alpha]_D^{25} +29.6^\circ$ in CHCl_3 . Trimethyl- α -methylglucosaminide hydrochloride with BzCl in aq. NaOH yields *N*-benzoyltrimethyl- α -methylglucosaminide (II), m.p. 162°, $[\alpha]_D^{25} +122.8^\circ$ in CHCl_3 , also formed from (I) by boiling with 2% $\text{HCl}\cdot\text{MeOH}$. Acetylation of triacetylbenzylglucosaminide hydrobromide (III) with $\text{Ac}_2\text{O}\cdot\text{AgOAc}$ in MeOH yields *tetra-acetyl- β -benzylglucosaminide*, m.p. 163°, $[\alpha]_D^{25} -38.3^\circ$ in CHCl_3 , methylated (Me_2SO_4 - NaOH) to *N*-acetyltrimethyl- β -benzylglucosaminide (IV), m.p. 174°, $[\alpha]_D^{25} -36.2^\circ$ in CHCl_3 , converted by $\text{HCl}\cdot\text{CH}_2\text{Ph}\cdot\text{OH}$ into the α -

isomeride, m.p. 138°, $[\alpha]_D^{25} +118.2^\circ$. With $\text{BzCl}\cdot\text{Ag}_2\text{CO}_3$ in H_2O (III) gives *N*-benzoyltriacetyl- β -benzylglucosaminide, m.p. 216°, $[\alpha]_D^{25} -6.4^\circ$ in CHCl_3 , methylated (Me_2SO_4 - $\text{NaOH}\cdot\text{COMe}_2$) to *N*-benzoyltrimethyl- β -benzylglucosaminide (V), m.p. 180°, $[\alpha]_D^{25} -21.75^\circ$ in CHCl_3 , converted by $\text{HCl}\cdot\text{CH}_2\text{Ph}\cdot\text{OH}$ into the α -isomeride (VI), m.p. 184°, $[\alpha]_D^{25} +123.2^\circ$ in CHCl_3 . When boiled with 2% $\text{HCl}\cdot\text{MeOH}$, (V) is unchanged, (VI) yields (II), and (IV) gives a mixture of trimethyl- α -methylglucosaminide and its *N*-Ac derivative. With 0.01N- HCl at 100°, *N*-acetyltrimethyl- β -methylglucosaminide (VII), (I), (IV), and (V) lose the glycosidic alkyl group, but the α -isomeride of (VII) is unchanged. Trimethyl- α -methylglucosaminide is methylated ($\text{MeI}\cdot\text{Ag}_2\text{O}$) to *trimethyl- α -methylglucosidyl-2-trimethylammonium iodide*, $[\alpha]_D^{25} +119.1^\circ$ in CHCl_3 , which is very resistant to alkalis, and on distillation yields *trimethyl-dimethylammonomethylglucoside*, b.p. 160° (bath)/0.03 mm. Triacetyl- β -methylglucosaminide hydrobromide with $\text{MeI}\cdot\text{Ag}_2\text{O}$ yields *trimethyl- β -methylglucosidyl-2-trimethylammonium iodide*, m.p. 105°, $[\alpha]_D^{25} -12.9^\circ$ in CHCl_3 , which is unchanged by boiling with 1% $\text{HCl}\cdot\text{MeOH}$, by which treatment 3-acetamidotrimethyl- α -methylglucoside is also unchanged.

J. D. R.

Dissymmetrical synthesis in the case of complex metallic salts.—See A., 1939, I, 212.

Protein metabolism. III. Synthesis of amino-acids containing isotopic nitrogen. R. SCHOENHEIMER and S. RATNER (J. Biol. Chem., 1939, 127, 301–313).—Two methods for the prep. of NH_2 -acids containing an excess of ^{15}N are described. (I) The corresponding keto-acids are reduced with H_2 in presence of Pd and NH_3 containing an excess of ^{15}N . In this way the following acids have been prepared: *dl*-alanine, *dl*-phenylalanine, *dl*-tyrosine, *dl*-norleucine, *dl*-glutamic acid, and *dl*-aspartic acid. (2) The appropriate α -Br-acid is treated with $\text{o}\cdot\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$ prepared from $\text{o}\cdot\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and NH_3 containing an excess of ^{15}N . The acids prepared in this way include glycine, deuteroleucine, and lysine. Deuterioisohexanoic acid, b.p. 200.2°, was prepared from isohexanoic acid and PtO_2 saturated with D_2 . Bromination by treatment with Br and red P followed by esterification yields an *Et* deuterio- α -bromoisohexanoate, b.p. 83–84°/10 mm. The *dl*-leucine finally obtained contained 3.87 at.-% D and 6.49 at.-% ^{15}N excess.

W. O. K.

Red coloration of ferric salts with glycine.—See A., 1939, I, 199.

***l*-(+)-Citrulline.** A. G. GORNALL and A. HUNTER (Biochem. J., 1939, 33, 170–172).—*l*-(+)-Arginine is incubated with arginase at 37° until the arginine has disappeared. The solution, conc. in vac. and decolorised, is boiled with CuO at p_{H} 7.0 and $\text{CO}(\text{NH}_2)_2$ added. The citrulline- Cu is then decomposed with H_2S giving *l*-(+)-citrulline, $[\alpha]_D^{25} +3.5^\circ$ in H_2O (hydrochloride, $[\alpha]_D^{25} +17.9^\circ$ in H_2O). A. L.

Octopine. I. Synthesis and titration curve of octopine. II. Nitrogenous extractives of squid and octopus muscle. III. Precursor of octopine in autolysing scallop muscle. J. L. IRVIN and D. W. WILSON (J. Biol. Chem., 1939, 127,

555—563, 565—574, 575—579).—Synthesis of octopino (I) (A., 1937, III, 295), m.p. 265° (decomp.) [picrate, m.p. 226° (decomp.); picrolonate, m.p. 236°], is repeated using a lower temp. and Akasi's method (A., 1937, II, 403) of separating the enantiomorphs. The titration curve of (I) closely resembles that of arginine (II). pK of (I) for the CO_2H are 1.36 and 2.40 and for the N 8.76 and nearly 13. M.p. are corr.

II. (I) [Cu salt , $(\text{C}_9\text{H}_{17}\text{O}_4\text{N}_4)_2\text{Cu}$, m.p. 223—227° (decomp.); *reineckate*; *Ni* compound, m.p. >290°, containing 87.1% of (I)] and (II) are isolated from the mantle and tentacle muscle of *Loligo pealii*, and the N partition in the muscle is determined. Taurine, adenine, hypoxanthine, betaine, (II), (I), and agmatine (modified isolation as phosphotungstate) are obtained from the tentacle muscle of *Octopus vulgaris*.

III. Fresh scallop muscle contains much (II) and little (I); the amount of (I) increases during autolysis at 0° at the expense of the (II), the change being faster in sliced than in hashed muscle. R. S. C.

Synthesis of dicholylcystine and cholylcysteic acid. S. F. VELICK, J. WHITE, and H. B. LEWIS (J. Biol. Chem., 1939, 127, 477—481).—Triformylcholic acid (prep. by HCO_2H at 60°, m.p. 206°, and pure SOCl_2 give the acid chloride, which with cystine Me_2 ester in CHCl_3 gives *bistriformylcholylcystine Me₂ ester* (I), m.p. 88—90°, and thence by NaOH in aq. dioxan etc. *dicholylcystine* $(\text{NH}_4)_2$ salt and the derived acid, which is less well obtained by way of the azide. Addition of Br to (I) in H_2O gives *Me triformylcholylcysteate*, converted by $\text{NH}_3\text{-MeOH}$ at room temp. into NH_4 β -*carbamyltaurocholate* or by NaOMe-MeOH at room temp. into *Na₂ cholylcysteate*.

R. S. C.

Oxamidedioxime. I. Determination of nickel.—See A., 1939, I, 219.

Sebacic acid methyl-, m.p. 98—99.5° (Et ester, m.p. 55°), and **propyl-monoamide**, m.p. 91—93°, and **NN'-dimethyl-**, m.p. 147.5—148.2°, and **-dipropyl-diamide**, m.p. 153—154°, and **suberic propylamide**, m.p. 91—92.3°.—See A., 1939, III, 172.

Monoanilide, m.p. 122° (Et ester, m.p. 65—66°), of adipic acid.—See A., 1939, III, 175.

Methyl-, m.p. 187—189°, and **dimethyl-colamine phosphate**, m.p. 75—80°.—See A., 1939, III, 183.

Urea derivatives. Quaternary ammonium compounds.—See B., 1939, 243.

Production of N-acylurethanes.—See B., 1939, 243.

Diacylcarbamides. II. Preparation and properties of diacylcarbamides derived from branched-chain aliphatic acids. R. W. STOUGH-TON, H. L. DICKSON, and O. G. FITZHUGH (J. Amer. Chem. Soc., 1939, 61, 408—410; cf. A., 1938, II, 352).—*isoButyryl-*, m.p. 175—176°, *isovaleryl-*, m.p. 204—205°, α -*methyl-n-butyryl-*, m.p. 179—180°, $\alpha\alpha$ -*dimethyl-n-propionyl-*, m.p. 147—148°, α -*ethyl-butyryl-*, m.p. 206—207°, α -*methylvaleryl-*, m.p. 152—153°, $\alpha\alpha$ -, m.p. 121—122°, and $\beta\beta$ -*dimethyl-n-butyryl-*, m.p. 173—174°, $\alpha\alpha$ -*dimethylvaleryl-*, m.p. 116—117°, and $\alpha\alpha$ -*dimethyl-n-hexoyl-*, m.p. 108—109°, -*carbamide* with the appropriate acyl halides give *N-acetyl-N'- $\alpha\alpha$ -dimethylpropionyl-*, m.p. 105—106°, -*N'- $\alpha\alpha$ -dimethylbutyryl-*, m.p. 118—119°, -*N'- $\beta\beta$ -dimethylbutyryl-*, m.p. 120—121°, -*N'- $\alpha\alpha$ -dimethylvaleryl-*, m.p. 63—64°, and -*N'- $\alpha\alpha$ -dimethylhexoyl-carbamide*, m.p. 77—78°, *N-isobutyryl-N'- α -methylbutyryl-*, m.p. 92—93°, -*N'- $\alpha\alpha$ -dimethylpropionyl-*, m.p. 170—171°, -*N'- α -ethylbutyryl-*, m.p. 75—76°, -*N'- α -methylvaleryl-*, an oil, and -*N'- $\alpha\alpha$ -dimethylbutyryl-carbamide*, m.p. 147—148°, *N-n-butyryl-N'- $\alpha\alpha$ -dimethylpropionyl-*, m.p. 71—72°, -*N'- α -ethylbutyryl-*, m.p. 57—58°, and -*N'- $\alpha\alpha$ -dimethylbutyryl-carbamide*, m.p. 66—67°, *N- α -methylbutyryl-N'- α -ethyl-*, m.p. 77—78°, and -*N'- $\alpha\alpha$ -dimethylbutyryl-carbamide*, m.p. 130—131°, *NN'-diisobutyryl-*, m.p. 111—112°, *NN'-diisovaleryl-*, m.p. 66—67°, *NN'-di-(α -methylbutyryl)-*, m.p. 87—88°, *NN'-di-($\alpha\alpha$ -dimethylpropionyl)-*, m.p. 206—207° (decomp.), *NN'-di-(α -ethylbutyryl)-*, m.p. 86—87°, and *NN'-di-($\alpha\alpha$ -dimethylbutyryl)-carbamide*, m.p. 163—164°, which are readily hydrolysed and weak anaesthetics. Esters of the *sec.* and *tert.* acids with $\text{CO}(\text{NH}_2)_2$ and NaOEt give only NaCNO and the corresponding amides. Pyrolysis of $\text{CO}(\text{NH-COPr}^i)_2$ at 200° gives $\text{Pr}^i\text{CO-NH}_2$, Pr^iCN , and CO_2 with smaller amounts of $\text{NH}(\text{COPr}^i)_2$ and $(\text{HCNO})_3$. M.p. are corr.

R. S. C.

Preparation of amino-nitriles and their quaternary ammonium derivatives. D. B. LUTEN, jun. (J. Org. Chem., 1939, 3, 588—597).— NH_2 -nitriles are obtained (a) by adding a slight excess of $\text{Na}_2\text{S}_2\text{O}_5$ to an aq. solution of the aldehyde followed after completion of the reaction by one equiv. of the amine and then by saturated aq. KCN or (b) by adding a solution of KCN to a conc. aq. solution of the amine hydrochloride followed by the desired aldehyde or ketone in about 30% excess. With method (a) good yields are obtained only from CH_2O and the simpler amines. In cases where the method is unsuccessful the failure appears due to the low rate or adverse equilibrium of the change, $\text{OH-CRR'-SO}_3^- + \text{NHR}''_2 \rightleftharpoons \text{NR}''_2\text{-CRR'-OH} + \text{HSO}_3^-$. Under the conditions adopted method (b) gives a good yield in many cases in which method (a) fails but it also fails in certain cases. There seems to be little relationship between the mol. wts. of the reactants and the ultimate yields, although NH_4Et_3 gives a much lower yield with each of the ketones employed than does NHMe_2 . Some of the aldehydic derivatives were obtained in low yields owing to withdrawal of the aldehydes by the competing aldol condensation reaction. The quaternary derivatives are obtained by adding the appropriate halide to the NH_2 -nitrile or by adding $\text{CH}_2\text{I-CN}$ to the appropriate *tert.* amine. The following individuals are described: $\text{NMe}_2\text{-CH}_2\text{-CN}$, b.p. 138°, 42°/21 mm. [methiodide, m.p. 228° (lit. 196°); *ethiodide*, m.p. 209°; *n-propiodide*, m.p. 95°; *isopropiodide*, m.p. 219°; *n-butyridide*, m.p. 86.5°; *n-hexadeciodide*]; $\text{NEt}_2\text{-CH}_2\text{-CN}$, b.p. 70°/23 mm., 53°/10 mm. (methiodide, m.p. 199°; *ethiodide*, m.p. 187°; *ethobromide*, m.p. 209°; *n-propiodide*, m.p. 195°; *n-butyridide*, m.p. 154°; *n-amylidide*, m.p. 125°; *alliodide*, m.p. 162°; $\text{NPr}^i_2\text{-CH}_2\text{-CN}$, b.p. 96°/23 mm., 78°/9 mm. (methiodide, m.p. 162°; *ethiodide*, m.p. 176°; *n-propiodide*, m.p. 179°); *di-n-butylaminoacetoneitrile*,

b.p. 85°/4 mm. (methiodide, m.p. 104°; *n*-butiodide, m.p. 131°); $\text{NBu}_2\text{CH}_2\text{CN}$, b.p. 87°/9 mm., 78—79°/4 mm.; *di-n*-amylaminoacetonitrile, b.p. 102—104°/4 mm.; *diisoamylaminoacetonitrile*, b.p. 93—94°/4 mm. (methiodide, m.p. 109°); *di-n*-octylaminoacetonitrile, b.p. 145—150°/3 mm.; *diethylaminoacetonitrile* β -hydroxyethiodide; *Et diethylaminoacetate cyanomethobromide*, m.p. 128°; *Et* β -dimethylaminopropionate cyanomethobromide, m.p. 102°, and the corresponding cyanomethiodide, m.p. 122°; α -dimethylaminopropionitrile, b.p. 59—61°/40 mm. (methiodide, m.p. 204°); $\text{NEt}_2\text{CHMeCN}$, b.p. 53°/11 mm. (methiodide, m.p. 202°); β -dimethylaminopropionitrile methochloride, m.p. 230°; $\text{NMe}_2\text{CHEtCN}$, b.p. 67—68°/23 mm. (methiodide, m.p. 176°; ethiodide, m.p. 135°); α -diethylaminobutyronitrile, b.p. 75°/16 mm. (methiodide, m.p. 184°); $\text{NMe}_2\text{CMe}_2\text{CN}$, b.p. 57°/25 mm., 46°/13 mm. (methiodide, m.p. 268°; ethiodide, m.p. ~250°); α -methyl-ethylaminoisobutyronitrile, b.p. 58°/14 mm.; $\text{NEt}_2\text{CMe}_2\text{CN}$, b.p. 72—74°/14 mm. (methiodide, m.p. 241°); γ -dimethylamino-*n*-butyronitrile methobromide, m.p. 226°; $\text{NMe}_2\text{CHPr}^n\text{CN}$, b.p. 70°/14 mm. (methiodide, m.p. 163°; ethiodide, m.p. 121°); α -diethylamino-*n*-valeronitrile, b.p. 95°/15 mm., 78°/4 mm. (methiodide, m.p. 132°); α -dimethylaminoisovaleronitrile, b.p. 61°/14 mm. (methiodide, m.p. 177°); α -diethylaminoisovaleronitrile, b.p. 69°/4 mm. (methiodide, m.p. 150°); α -dimethylamino- α -methyl-*n*-butyronitrile, b.p. 63°/12 mm. (methiodide, m.p. 216°); α -diethylamino- α -methyl-*n*-butyronitrile, b.p. 78°/16 mm. (methiodide, m.p. ~220°); α -diethylamino-*n*-hexonitrile, b.p. 91°/9 mm. (methiodide, m.p. 116°); α -dimethylamino- α -methyl-*n*-valeronitrile, b.p. 75°/10 mm. (methiodide, m.p. 165°); α -diethylamino- α -methyl-*n*-valeronitrile, b.p. 103°/21 mm., 80—85°/5 mm. (methiodide, m.p. 119°); $\text{NMe}_2\text{CMePr}^n\text{CN}$, b.p. 63°/7 mm. (methiodide, m.p. 188°); $\text{NMe}_2\text{CEt}_2\text{CN}$, b.p. 69—73°/10 mm. (methiodide, m.p. 191°); $\text{NEt}_2\text{CH}(n\text{-C}_6\text{H}_{13})\text{CN}$, b.p. 113—115°/13 mm.; α -dimethylamino- α -methyl-*n*-heptonitrile, b.p. 104—105°/10 mm., (methiodide, m.p. 199°); $\text{NPhMeCH}_2\text{CN}$, b.p. 138—141°/9 mm., $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2\cdot\text{I}\cdot\text{CH}_2\text{CN}$; *benzylmethylaminoacetone* methobromide, m.p. 158°; $\text{NMe}_2\text{CHPhCN}$, b.p. 90°/6 mm.; $\text{NEt}_2\text{CHPhCN}$, b.p. 122—124°/9 mm.; piperidinoacetonitrile, b.p. 83°/9 mm. (methiodide, m.p. 206°; ethiodide, m.p. 183°; *n*-propiodide, m.p. 152°); *Et piperidinoacetate cyanomethobromide*, m.p. 154°.

H. W.

Reversibility of the glycerophosphoric change.
—See A., 1939, I, 205.

Preparation of calcium glucose-3-phosphate from dibrucine glucose-3-phosphate. S. A. LOUGH and V. E. SPENCER (J. Org. Chem., 1939, 3, 541—542).—The action of $\text{Ca}(\text{OH})_2$, dissolved or in suspension, on glucose-3-phosphoric acid gives compounds containing more Ca and less P than required for the simple salt. *Ca glucose-3-phosphate* is prepared by addition of the stoichiometrical amount of solid $\text{Ca}(\text{OH})_2$ to a well-stirred suspension of dibrucine glucose-3-phosphate in H_2O ; brucine is removed by filtration and the salt is pptd. by adding EtOH to the filtrate.

H. W.

Telluromercaptans. A. BARONI (R. C. Atti Accad. Lincei, 1938, [vi], 27, 238—242).— H_2Te in EtOH- NaOEt with RBr ($\text{R} = \text{Me}$, Et, Pr^n , Bu^n) yields the corresponding telluromercaptan RTeH ; $\text{R} = \text{Me}$, b.p. 57°, Et, b.p. 90°, Pr^n , b.p. 121°, Bu^n , b.p. 151°. An apparatus for the prep., purification, and distillation of the telluromercaptans as a continuous operation in H_2 is described. F. O. H.

Action of halides on magnesium compounds. G. VAVON, J. CALIN, and J. FOUCHIER (Compt. rend., 1939, 208, 203—205).—The time necessary for 40% reaction between MgEtBr and various halides and between allyl bromide and various Mg compounds in Bu_2O at 65° and 35° (equimol. concns.) is determined. MgRBr reacts much more slowly with *n*-org. halides than with *sec.* and *tert.* compounds; a double linking in the org. halide facilitates the reaction. The chlorides react least and the iodides most easily; bromides are intermediate. The difference in reaction rate using MgRBr , MgRCl , or MgRI is small, but the bromide reacts most easily. The reaction is at first rapid and then slow (migration of Mg) (cf. Prévost, A., 1932, 41; Urien, A., 1934, 640).

J. L. D.

Reaction of carbon suboxide with magnesium methyl iodide. J. H. BILLMAN and C. M. SMITH (J. Amer. Chem. Soc., 1939, 61, 457—458).—Only 1 mol. of MgMeI reacts with C_3O_2 in Et_2O , yielding $\text{CO:C:Me}\cdot\text{OMgI}$, which, after hydrolysis, condenses to give 2 : 4 : 6 : 1 : 3 : 5- $\text{C}_6\text{Ac}_3(\text{OH})_3$ as sole product.

R. S. C.

Yields of stibines and arsines. J. SEIFTER (J. Amer. Chem. Soc., 1939, 61, 530—531).—A mixture of const. b.p. (min. b.p. 72—74°) was obtained by distilling the product of the prep. of SbMe_3 in Bu_2O . Prep. of SbBu_3 in 70% yield and of AsBu_3 in 50% yield is recorded.

R. S. C.

Mechanism of catalytic hydrogenation of phenol [to hydrocarbons] under high pressure. IV. S. ANDŌ (J. Soc. Chem. Ind. Japan, 1938, 41, 386—390B; cf. A., 1933, 498).—The products of hydrogenation of PhOH , C_6H_6 , and cyclohexane at 430° or 471°/~240 atm. (rotating autoclave) in presence of MoO_3 or $\text{MoO}_3 + \text{S}$ indicate that cyclohexane and methylcyclopentane are formed from PhOH not only via C_6H_6 , but also via cyclohexanol and cyclohexene, although neither of these two intermediates has been isolated (cf. A., 1932, 51; B., 1932, 762; A., 1933, 1152).

A. R. PE.

Hydrogenation-cracking of diphenylene oxide and some related compounds. C. C. HALL and C. M. CAWLEY (J.S.C.I., 1939, 58, 7—13).—Diphenylene oxide (I) is fairly stable at 450°/200 atm. H_2 in presence of supported Mo catalyst; 40—60% is unchanged after heating for 2 hr. Complete conversion is obtained at 500°. It is less stable in the presence of a pelleted MoS_2 catalyst, 14% remaining unchanged at 450°, and 35% at 350°. The stability of Ph_2 is very similar, but 2-hydroxydiphenyl (II) is much less stable and is completely deoxygenated at 450° in presence of the supported catalyst. 2 : 2'-Dihydroxydiphenyl (III) is readily converted into (I) and (II). At low temp. the initial decomp. product of (I) is *o*-cyclohexylphenol (IV) and at high

temp. (II) is formed; both (II) and (IV) are converted into phenylcyclohexane (V) to a large extent, but (II) also yields some Ph_2 . Ph_2 undergoes scission to C_6H_6 , or is hydrogenated to (V), which undergoes scission to C_6H_6 and cyclohexane (VI) or is hydrogenated to dicyclohexyl which then yields (VI).

Infra-red spectra of naphthalene, 1- and 2-methylnaphthalene, quinoline, and isoquinoline.—See A., 1939, 1, 179.

New hydrocarbon from juniper oil. P. CASPARIS and W. FREUND (Pharm. Acta Helv., 1939, 14, 1—8).—Oil from juniper berries collected in the Tyrol and from Italian fruits gave by fractional distillation 0.17—0.345% of *junene* (I), $\text{C}_{10}\text{H}_{16}$, b.p. 164—166°/760 mm., 53—55°/8 mm., α_D^{20} (1 dm.) +19.6° to +20.1°, possessing strong diuretic properties; a solution in Ac_2O gave a red coloration with H_2SO_4 . Reduction (H_2 , Pd-BaSO₄, AcOH) of (I) gave *dihydrojunene*, $\text{C}_{10}\text{H}_{18}$, b.p. 170°/760 mm., 58—61°/8 mm., α_D^{20} (5 cm.) -6.5°. With HCl in AcOH (I) gave an additive product, b.p. 76—86°/8 mm., α_D^{20} -0.3°, and no cryst. products with Br, NOCl, or HI, and did not react with BzO_2H . It is probably a cyclopentene derivative similar to but not identical with the chamene of Kafaku *et al.* (B., 1931, 565). The juniper oils contained α -pinene, camphene, and cadinene and, from the consts. of the terpene fraction, 5—15% of (I). T. F. W.

β -Nitrostyrene in the diene synthesis. C. F. H. ALLEN and A. BELL (J. Amer. Chem. Soc., 1939, 61, 521—522).— $\text{CHPh}\cdot\text{CH}\cdot\text{NO}_2$ and the appropriate diene give 4-nitro-5-phenyl-1:2-dimethyl- (I) (82%), m.p. 96°, 4-nitro-5-phenyl-1- (or 2-)methyl- (7%), m.p. 52°, 4-nitro-1:2:5-triphenyl- (II) (9%), m.p. 175°, and 4-nitro-3:5:6-triphenyl- (40%), m.p. 130°, Δ^1 -cyclohexene; (II) is accompanied by a hydrocarbon (5%), $\text{C}_{24}\text{H}_{20}$, m.p. 77°. In KOH, but not in neutral solution, (I) gives the 4-Br-derivative. Methylenanthrone gives N oxides, *Bz*-1-phenylbenzanthrone (25%), and its *Bz*-2- NO_2 -derivative (3%), m.p. 255° (oxidised to 1-benzoylanthraquinone). Tetracyclone gives C_6HPh_5 . Phellandrene, cyclopentadiene, and cyclohexadiene give adducts, $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}$ (45%), b.p. 190°/1 mm., $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}$ (95%), b.p. 145°/1 mm., and $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}$, (20%), b.p. 138—142°/1 mm., respectively. R. S. C.

Substitution process. W. HÜCKEL (Österr. Chem.-Ztg., 1939, 42, 105—109, 121—125).—Comparison of theory (Meer and Polanyi; Ingold and Hughes) with experience is at present possible only with changes of the bimol. type with negative mechanism. All such substitutions are accompanied by Walden inversion. The most important types of change are: replacement of halogen by halogen ion; substitution of halogen by OH; formation of ethers from halides and alkoxides; production of acetates from KOAc and toluene-*p*-sulphonates in EtOH. Study of the interaction of HNO_2 and the amines derived from decahydronaphthalene shows that the steric course of substitution depends greatly on the fine structure of the mol. and is influenced by the steric arrangement of parts of the mol. distant from the asymmetry centre involved in substitution. In

those cases in which >50% of hydrocarbon is produced, the formation of alcohol is accompanied by almost complete Walden inversion although a little configuratively-similar alcohol is produced. On the other hand an alcohol formed from an amine almost without hydrocarbon has, in seven out of eight cases, the same configuration as the amine and the stereoisomeric alcohol is not formed in appreciable amount. In the first cases the alcohols exhibit marked steric hindrance whereas in the second case they do not. Ingold's views on substitution are critically discussed. Criticisms of the older and more recent views of the nitration, sulphonation, and halogenation of aromatic compounds lead to the conclusion that a single scheme, applicable to all aromatic substitutions, cannot at present be advanced. H. W.

Rôle of sulphuric acid [in sulphonation, nitration, etc].—See A., 1939, 1, 211.

Emulsification and chemical reaction.—See A., 1939, 1, 204.

Preparation of *m*-dinitrobenzene. S. V. SHAH and D. G. PISHAWIKAR (J. Chem. Educ., 1939, 16, 35; cf. A., 1937, II, 406).— NaNO_3 can replace HNO_3 without loss in yield, and with a considerable reduction in the cost of materials. L. S. T.

Substitution of aromatic hydrocarbons. F. ASINGER (J. pr. Chem., 1939, [ii], 152, 1—8; cf. A., 1934, 878).—Passage of Cl_2 into CH_2PhBr causes rise of temp. to 100° and escape of Br. At 0° in presence of a little I, the total halogen content is that required for $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Br}$ but Br has been partly displaced from the side-chain to the nucleus; at 25° this effect is somewhat less marked. Bromination of CH_2PhCl causes much displacement of Cl by Br; Cl is evolved as HCl and does not enter the nucleus. Passage of Cl_2 through $\text{C}_6\text{Br}_6 + p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ at 200° gives unchanged *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$; the gaseous products are free from Br. H. W.

Tetra- and penta-chloroethylbenzene.—See B., 1939, 243.

Friedel-Crafts reactions: *n*-octadecylbenzene and diacylations. H. GILMAN and J. A. V. TURCK, jun. (J. Amer. Chem. Soc., 1939, 61, 478—479).—Only *n*- $\text{C}_{18}\text{H}_{37}\text{Ph}$ (identified as sulphonamide) is obtained from $\text{C}_6\text{H}_6 + n\text{-C}_{18}\text{H}_{37}\text{Hal} + \text{AlCl}_3$, *n*- $\text{C}_{18}\text{H}_{37}\text{I} + \text{PhI} + \text{Na}$, or by Clemmensen reduction of stearophenone (I). In the Friedel-Crafts reaction with (I) and *n*- $\text{C}_{17}\text{H}_{35}\cdot\text{COCl}$ in PhNO_2 , no distearoylbenzene is produced; $\text{CO}(\text{C}_{17}\text{H}_{35})_2$, *o*- and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ are formed. R. S. C.

Polymethylbenzenes. XXIII. Preparation and physical properties of 3- and 5-ethyl- ψ -cumenes and of ethylmesitylene. L. I. SMITH and M. A. KRESS (J. Amer. Chem. Soc., 1939, 61, 284—288; cf. A., 1939, II, 102).—1:2:4:5- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{SO}_3\text{H}$ and Br-aq. HCl give 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}_3\text{Br}$ (60%) and 1:2:4:3:5- $\text{C}_6\text{HMe}_3\text{Br}\cdot\text{SO}_3\text{H}$, hydrolysed by 50% H_2SO_4 and steam at 175—180° to ψ -cumene, 1:2:4:3- $\text{C}_6\text{H}_2\text{Me}_3\text{Br}$, and other products. The appropriate Grignard reagents (prepared with the aid of EtBr) and Et_2SO_4 in Et_2O give 31—52% of

1 : 3 : 5 : 2- $C_6H_2Me_3Et$ (I), b.p. $210^\circ/725$ mm., m.p. -15.56° , 5- (II), b.p. $210^\circ/725$ mm., m.p. -13.58° , and 3-ethyl- ψ -cumene (III), b.p. $214^\circ/725$ mm., m.p. $<-50^\circ$, with 14–35% of $C_6H_3Me_3$. (I) and (II) are also obtained (Clemmensen) from 1 : 3 : 5 : 2- (74%) and 1 : 2 : 4 : 5- $C_6H_2Me_3COMe$ (77.2%), respectively. With $H_2SO_4-HNO_3$ (d 1.5) in $CHCl_3$ (III) gives the 5 : 6- $(NO_2)_2$, m.p. $79-80^\circ$, and thence by $SnCl_2-HCl-EtOH$ the $(NH_2)_2$ -derivative (IV), m.p. $84-85^\circ$, or by $SnCl_2-HCl-AcOH$ 2 : 4 : 6 : 7-tetramethyl-5-ethylbenziminazole, m.p. 205.5° . (IV) yields 10 : 12 : 13-trimethyl-11-ethylphenanthraphenazine, m.p. 242° . When treated successively with oleum, H_2O , and Br, (III) gives the 5 : 6- Br_2 -derivative, m.p. $65-66^\circ$. $KMnO_4-K_2CO_3$ converts (III) into 1 : 2 : 3 : 4- $C_6H_2(CO_2H)_4$, but 1 : 2 : 3 : 5- $C_6H_2(CO_2H)_4$ could be obtained from (I) only by long heating with $KMnO_4-NaOH$. R. S. C.

Carotenoids from lucerne silage etc.—See A., 1939, III, 343.

Volatile plant substances. VIII. Synthesis of vetivazulene. A. S. PFAU and P. A. PLATTNER (Helv. Chim. Acta, 1939, 22, 202–208).—Gradual addition of 2 : 5 : 1- $C_6H_3Me_2\cdot CH_2Cl$ to $CNaPr^s(CO_2Et)_2$ in xylene followed by protracted boiling of the mixture gives Et, 2 : 5-dimethylbenzylisopropylmalonate, b.p. $160-165^\circ/3$ mm., hydrolysed with difficulty to the corresponding acid, which when distilled in a vac. gives β -2 : 5-dimethylphenyl- α -isopropylpropionic acid, m.p. $69-70^\circ$. The corresponding chloride, b.p. $135^\circ/3$ mm., is cyclised by $AlCl_3$ in C_6H_6 to 4 : 7-dimethyl-2-isopropylindan-1-one, b.p. $146^\circ/3$ mm., which in consequence of steric hindrance does not give an oxime or a semicarbazone, but is reduced by Na and EtOH to 4 : 7-dimethyl-2-isopropylindan-1-ol, m.p. $98-99^\circ$. It is reduced (Clemmensen) to 4 : 7-dimethyl-2-isopropylindane (I), b.p. $108-110^\circ/3$ mm., m.p. $23-24^\circ$, oxidised to $C_6H_2(CO_2H)_4$ and nitrated to 5 : 6-dinitro-4 : 7-dimethyl-2-isopropylindane, m.p. 137° . Gradual addition of $CHN_2\cdot CO_2Et$ to (I) at 130° followed by heating the mixture to 160° and distillation yields a product which is hydrolysed, decarboxylated, and dehydrogenated (Pd-C) to vetivazulene [4 : 8-dimethyl-2-isopropyl-dicyclo[0,3,5]-decapentaene], m.p. $32-33^\circ$, identical with the natural product. H. W.

Nitration of naphthalenesulphonic acids. I, II. R. LANTZ (Bull. Soc. chim., 1939, [v], 6, 280–289, 289–302; cf. A., 1936, 62, 197).—2- $C_{10}H_7\cdot SO_3Na$ and 100% H_2SO_4 at room temp. for 2 days give 1 : 6- $C_{10}H_6(SO_3H)_2$, purified through 1 : 6- $C_{10}H_6(SO_2Cl)_2$. 2 : 7-, 2 : 6- (I), and 1 : 5- $C_{10}H_6(SO_3Na)_2$ and 100% H_2SO_4 at 100° (1 : 5- at 60°), then 60% oleum, afford 1 : 3 : 6-, 2 : 4 : 6-, and 1 : 3 : 5- $C_{10}H_5(SO_3H)_3$, respectively. (I) and 59% oleum in $H_2SO_4\cdot H_2O$ at 180° for 8 hr. give 1 : 3 : 5 : 7- $C_{10}H_4(SO_3H)_4$ (hygroscopic Na salt). Details of nitration of Na naphthalenesulphonates with $H_2SO_4-HNO_3$ under varied conditions are recorded; HNO_3 used is estimated by difference before and after nitration. Max. speed of nitration is obtained usually (at room temp.) with $\sim 90\%$ H_2SO_4 ; in general, under these conditions, the total no. of SO_3H+NO_2 in the final product is 4. With cold

100% H_2SO_4 , however, the total no. of substituents is 3, i.e., $C_{10}H_6(SO_3H)_2$ are mononitrated and $C_{10}H_5(SO_3H)_3$ are practically unaffected; under these conditions, NO_2 -derivatives of 1 : 5- and 1 : 6- $C_{10}H_6(SO_3H)_2$ are transformed appreciably into products (possibly nitrosonaphtholsulphonic acids) which do not nitrate further, but those of the 2 : 6- and 2 : 7-acids undergo further slow nitration at $60-80^\circ$ to $(NO_2)_2$ -derivatives. 1 : 6- $C_{10}H_6(SO_3H)_2$ thus gives the 3- NO_2 - or 3 : 8- $(NO_2)_2$ -derivative; 2 : 7- $C_{10}H_6(SO_3H)_2$ affords the 4- NO_2 - or 4 : 5- $(NO_2)_2$ -compound; the 2 : 6-acid gives the 8- NO_2 - or 4 : 8- $(NO_2)_2$ - and the 1 : 5-acid a 4(or 3)- NO_2 - or 3 : 8- $(NO_2)_2$ -derivative. 1 : 3 : 6-, 2 : 4 : 6-, and 1 : 3 : 5- $C_{10}H_5(SO_3H)_3$ all give 8- NO_2 -derivatives. Fixation of NO_2 is little altered with variation in time and, within certain limits, with excess of HNO_3 . Large excess of HNO_3 and prolonged time give slight dinitration with the 1 : 3 : 5-acid. The 1 : 6- and 2 : 7-di- and the 1 : 3 : 6-tri-sulphonic acids nitrate completely in presence of 90% H_2SO_4 with slight excess of HNO_3 (note final orientation, 1 : 3 : 6 : 8; cf. Vesely *et al.*, A., 1923, i, 911). The 1 : 5-, 2 : 6-, 1 : 3 : 5-, and 2 : 4 : 6-derivatives require a large excess of HNO_3 to give analogous results. The result of Fierz (A., 1921, i, 409) that no NO_2 -derivative could be obtained from 1 : 3 : 5 : 7- $C_{10}H_4(SO_3H)_4$ is confirmed.

A. T. P.

Free radicals and radical stability. IV. Diphenyl-3-acenaphthylmethyl. S. T. BOWDEN and W. E. HARRIS (J.C.S., 1939, 307–310).—Ph 3-acenaphthyl ketone (modified prep.; cf. Graebe *et al.*, A., 1903, i, 408) and $MgPhBr$ give diphenyl-3-acenaphthylcarbinol (I), m.p. 196° (corresponding methane, m.p. 167°), prepared less readily from 3-bromoacenaphthene, activated Mg, and $COPh_2$. The basicity of (I) compared with that of 1- $C_{10}H_7\cdot CPh_2\cdot OH$ ($=1$) is 1 : 3, and the halochromic salts of (I) are bluer. (I) and $AcCl-C_6H_6$ or dry $HCl-C_6H_6$ (+ $CaCl_2$) give the chloride (II), m.p. 141° ; $AcBr-C_6H_6$ affords the bromide, m.p. 135° . Diphenyl-3-acenaphthylmethyl is isolated from (II) and mol. Ag in C_6H_6 , as crystals, m.p. 155° (vac.) (deep bluish-red in C_6H_6 ; deep bluish-green in liquid SO_2); air oxidation gives the peroxide, m.p. 167° (not completely colourless). Radical stability in $PhNO_2$ (bluish-green solutions) is approx. the same as that of diphenyl- α -naphthylmethyl (cf. Schlenk *et al.*, A., 1913, i, 34). Thermal decomp. of diphenyl- α -naphthylmethyl formate at 99° is slow, with formation of CO_2 and the corresponding methane, but the formate of (I) gives no CO_2 and no methane derivative is isolated.

A. T. P.

Condensation of benzylidene chloride with o-xylene. E. DE B. BARNETT (J.C.S., 1939, 348).— $CHPhCl_2$ and o-xylene, with $AlCl_3$ in $C_2H_2Cl_4$, give a little 9 : 10-diphenyl-2 : 3 : 6 : 7-tetramethylantracene, m.p. 312° (cf. Ellison and Hey, A., 1939, II, 14).

A. T. P.

Dehydrogenation. II. S. C. SENGUPTA (J. pr. Chem. 1939, [ii], 152, 9–19).—Gradual addition of $C_{10}H_8$ and α -dimethylsuccinic anhydride (I) to $AlCl_3$ in $PhNO_2$ at 0° and keeping the mixture at room temp. gives γ -keto- γ -1-naphthyl- α -dimethylbutyric acid

(II), m.p. 190—191° (oxidised by NaOBr to α -C₁₀H₇·CO₂H), and γ -keto- γ -2-naphthyl- α -dimethylbutyric acid (III), m.p. 170°, oxidised to β -C₁₀H₇·CO₂H. (II) is reduced (Clemmensen) to γ -1-naphthyl- α -dimethyl-n-butyric acid, m.p. 99—101° (the *Et* ester, b.p. 116—118°/6 mm., could not be condensed with Et₂C₂O₄ and KOEt), cyclised by H₂SO₄ at 100° to 1-keto-2:2-dimethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 69°; this is reduced (Zn-Hg-HCl) to 2:2-dimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 161—163°/6 mm., dehydrogenated by Se at 250—300° and then at 300—340° to 2-methylphenanthrene, m.p. 55—56° (picrate, m.p. 117—118°). (III) is reduced (Clemmensen) to γ -2-naphthyl- α -dimethylbutyric acid, b.p. 200—205°/5 mm., m.p. 133—135°, cyclised by H₂SO₄ at 100° to 4-keto-3:3-dimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 185—187°/8 mm., whence 3:3-dimethyl-1:2:3:4-tetrahydrophenanthrene, b.p. 155—157°/7 mm., dehydrogenated to impure 3-methylphenanthrene, m.p. 85° after softening at 61°, and other hydrocarbons. 1-C₁₀H₇·Me and (I) similarly afford γ -keto- γ -4-methyl-1-naphthyl- α -dimethylbutyric acid (IV), m.p. 202—203° [*Me* ester (V), m.p. 77°], oxidised by NaOCl to 4:1-C₁₀H₆·Me·CO₂H. (IV) cannot be reduced (Clemmensen) whereas (V) is transformed (after hydrolysis) into γ -4-methyl-1-naphthyl- α -dimethylbutyric acid, m.p. 105—106°. This is cyclised (H₂SO₄) to 1-keto-2:2:9-trimethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 123°, reduced to 2:2:9-trimethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 90—91°, which is dehydrogenated to 2:9-dimethylphenanthrene, m.p. 55—56° (picrate, m.p. 136—137°). H. W.

Polycyclic aromatic hydrocarbons. XX. J. W. COOK and C. G. M. DE WORMS (J.C.S., 1939, 268—271).—Cyclisation of CO(C₁₀H₇)₂ with AlCl₃-NaCl at 100° gives 1:2:5:10-dibenz-9-anthrone, oxidised by CrO₃-AcOH to 1:2-benzanthraquinone-5-carboxylic acid, m.p. 295—296° (*Me* ester, m.p. 163—165°) (oxidised by KMnO₄ to anthraquinone-1:2:5-tricarboxylic acid), which with SnCl₂-HCl-AcOH gives 1:2-benz-5-anthraic acid (I), m.p. 286—287° [the *amide*, m.p. 309—310°, and boiling *o*-C₆H₄(CO)₂O give the *nitrile*, m.p. 190—191°]. The *Et* ester, m.p. 89—90°, of (I) and MgMeI give a carbinol, dehydrated (EtOH-picric acid) to 5-isopropenyl-1:2-benzanthracene (II) (picrate, m.p. 141—142°). A dil. solution in C₆H₆ of its *s*-C₆H₃(NO₂)₃ complex, m.p. 155°, undergoes fission with activated Al₂O₃ (cf. Fieser *et al.*, A., 1938, II, 356). (II) is hydrogenated (Pt-black; EtOH) to 5-isopropyl-1:2-benzanthracene, m.p. 111—112° (picrate, m.p. 166·5—167·5°; *s*-C₆H₃(NO₂)₃ complex, m.p. 168·5—169·5°), oxidised by Na₂Cr₂O₇-AcOH to the benzantraquinone, m.p. 80—82°.

[By J. W. COOK and J. IBALL (cf. A., 1938, II, 227)]. Purified 8-methyl-1:2-benzanthracene (cryst. form examined) has new m.p. 117—118° (picrate, new m.p. 158—159°; *s*-C₆H₃(NO₂)₃ complex, new m.p. 167—168°). A. T. P.

Synthesis of 10-alkyl derivatives of 9-methyl-1:2-benzanthracene. B. M. MICHAÏLOV and N. G. TSCHERNOVA (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 579—581).—*o*-(α -1-Naphthylethyl)benzoic acid with ZnCl₂ at 180° yields 9-methyl-1:2-benz-1 (A., II.)

anthrone-10, m.p. 106·4—107·2°, which, with the appropriate Mg alkyl halide yields 9:10-dimethyl- (picrate, m.p. 112·2—113·2°), 9-methyl-10-ethyl-, m.p. 70—71·5° (dipicrate, m.p. 116—116·8°), 9-methyl-10-n-propyl-, m.p. 99—101° (dipicrate, m.p. 95—98°), and 9-methyl-10-n-butyl-1:2-benzanthracene, m.p. 71—72° (dipicrate, m.p. 104·6—105·8°). J. D. R.

Triterpenes. XLIII. Synthesis of 1:10-dimethyl-, 1:2:8- and 1:2:10-trimethyl-, and 1:2:9:10-tetramethylpicene. L. RUZICKA and K. HOFMANN [with, in part, E. HARDEGGER, G. HOEPE, A. MARXER, and J. FREY] (Helv. Chim. Acta, 1939, 22, 126—134).—1:8-Dimethylpicene, the picene derivative obtained by the dehydrogenation of pentacyclic triterpenes, can be certainly distinguished from the homologous picenes which would result by the dehydrogenation of a symmetrically constructed C skeleton. 1-Keto-5-methyl-1:2:3:4-tetrahydronaphthalene (I) is converted by Zn and CH₂Br·CO₂Et in anhyd. C₆H₆ followed by distillation in presence of a little I into Et 5-methyl-3:4-dihydro-1-naphthylacetate, b.p. 122—128°/0·1 mm., reduced by Na and abs. EtOH to β -5-methyl-1:2:3:4-tetrahydro-1-naphthylethyl alcohol, b.p. 107—109°/0·1 mm. (3:5-dinitrobenzoate, m.p. 91—92°). This yields the bromide (II), b.p. 96—97°/0·1 mm., the Mg derivative of which with (I) yields a product dehydrogenated (Pd-C at 320—330°) to $\alpha\beta$ -di-5-methyl-1-naphthylethane, m.p. 115—117° after softening, cyclised by AlCl₃ in CS₂ at room temp. to 1:10-dimethylpicene, m.p. 380—381° (corr.). The Mg compound of (II) and 1-keto-5:6-dimethyl-1:2:3:4-tetrahydronaphthalene (III) give a product which is distilled and then dehydrogenated (Pd-C at 320—330°) to α -5-methyl-1-naphthyl- β -5':6'-dimethyl-1'-naphthylethane, m.p. 128—129°, cyclised (AlCl₃-CS₂) to 1:2:10-trimethylpicene, m.p. 380—381° (corr.). Mg β -7-methyl-1:2:3:4-tetrahydro-1-naphthylethyl bromide and (III) give a product which is distilled and dehydrogenated to α -7-methyl-1-naphthyl- β -5':6'-dimethyl-1'-naphthylethane, m.p. 107—110° after softening, whence 1:2:8-trimethylpicene, m.p. 309—310° (corr.). (III) is converted by Zn and CH₂Br·CO₂Et in C₆H₆ into Et 5:6-dimethyl-3:4-dihydro-1-naphthylacetate, b.p. 105—110°/0·1 mm., reduced to β -5:6-dimethyl-1:2:3:4-tetrahydro-1-naphthylethyl alcohol, b.p. 128—132°/0·02 mm. 33% HBr-AcOH at 100° transforms this into the bromide, b.p. 130—133°/0·1 mm., the Grignard compound from which with (III) (as above) affords $\alpha\beta$ -di-5:6-dimethyl-1-naphthylethane, m.p. 163—165°, whence 1:2:9:10-tetramethylpicene, m.p. 400—401° (corr.). H. W.

Vinylamines. I. W. KRABBE and K. H. SCHMIDT [with E. POLZIN] (Ber., 1939, 72, [B], 381—390).—Under strictly defined conditions OH·CPh₂·CH₂·NH₂ (I) is transformed by Et₂C₂O₄ into diphenyl-N-ethoxalylamidomethylcarbinol, m.p. 128—129°, converted by boiling CO₂Et·COCl (II) into N-ethoxalyl- $\beta\beta$ -diphenylvinylamine (III), m.p. 128—129°, obtained directly but in poorer yield from (I) and (II). Hydrolysis of (III) with KOH-MeOH affords $\beta\beta$ -diphenylvinylamine (IV), m.p. 141·5—142·5° [picrate, m.p. 273° (partial decomp.); unstable hydrochloride].

(IV) is somewhat unstable and is best identified by its red halochromism in conc. H_2SO_4 . This effect is also shown by (I) owing to its transformation into (IV), which can thus be effected preparatively. The most characteristic property of (IV) is its sensitiveness to acids. Thus (IV) suspended in MeOH is almost instantaneously converted by HCO_2H into di- β -diphenylvinylamine. A solution of (IV) in dioxan can be preserved unchanged for days whereas in ligroin there is gradual formation of COPh_2 , HCN , and resin. Decomp. is greatly accelerated by the presence of impurities. (IV) does not decolorise Br in CHCl_3 and only slowly reduces KMnO_4 in aq. Na_2CO_3 . Ozonisation of (IV) in cyclohexane and decomp. of the ozonide with H_2O yields COPh_2 and $\text{HCO}\cdot\text{NH}_2$. H. W.

Action of dimethylamine on 3:4-dibromo-1-methylcyclohexane. J. GUTMAN (Compt. rend., 1939, 208, 524—525; cf. A., 1939, II, 56).—3:4-Dibromo-1-methylcyclohexane with NHMe_2 at 120—130° under pressure affords 3-dimethylamino-1-methyl- Δ^4 -cyclohexene (90%), b.p. 65°/25 mm. (hydrochloride, m.p. 125—126°; methiodide, m.p. 200—201°; picrate, m.p. 169—170°), reduced (H_2 -Raney Ni) to a mixture, b.p. 85°/50 mm., of *cis*- (picrate, m.p. 190—191°) and *trans*-3-dimethylamino-1-methylcyclohexane (picrate, m.p. 178—179°); the respective amines are also obtained by reduction of 3-methylcyclohexanoneoxime in acid and alkaline solution and subsequent methylation. The picrates of *cis*- and *trans*-4-dimethylamino-1-methylcyclohexane have m.p. 193° and 194°, respectively. J. L. D.

Action of di-(β -hydroxyethyl)amine, methylamine, and ethylamine on halogenonitrobenzenes. K. F. WALDKÖTTER (Rec. trav. chim., 1939, 58, 132—138).—When boiled with $\text{NH}[(\text{CH}_2)_2\text{OH}]_2$ in EtOH, 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ yields 2:4-dinitro-, m.p. 99° (diacetate, m.p. 77°; dinitrate, m.p. 103°), whilst 1:2:4:6- $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$ gives 2:4:6-trinitro-*di*- β -hydroxyethylaniline, m.p. 245° (mononitrate, m.p. 198°), together with β -hydroxyethyl- β' -2:4:6-trinitrophenoxyethylamine, m.p. 154°, which gives picric acid on nitration. 1:3:4:6- $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)_2$ similarly yields 4:6-dinitro-1:3-bis(di- β -hydroxyethylamino)benzene, m.p. 126°. Condensation (sealed tubes) of NH_2Me and NH_2Et with 1:4:2- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$, 1:3:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$, 1:3:4:6- and 1:3:4:5- $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)_3$, 3:5:1:4- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Cl}\cdot\text{OMe}$, and the appropriate Br-compounds, followed by acetylation or nitration of some of the products formed, gave the following compounds, having the m.p. given: 4-chloro-2-nitro-*NN*-acetyl-methyl-, 92°, and -ethyl-aniline, 47°, and the 4-Br-compounds, 116° and 57°, respectively; 4-chloro- (Ac derivative, 134°) and -bromo-2:6-dinitro-*N*-methylaniline (Ac derivative, 103°); 4-chloro-, 101° (Ac derivative, 73°), and -bromo-2:6-dinitro-*N*-ethylaniline, 90° (Ac derivative, 91°); 5-chloro-2-nitro-*NN*-acetyl-methyl-, 87°, and -ethyl-aniline, 108°, and the 5-Br-compounds, 112° and 129°, respectively; 4:6-dinitro-1:3-di-(methylamino)- (+1EtOH), 160—170° (Ac₂ derivative, 173°), and -(ethylamino)-benzene (+1EtOH), 90—110° (Ac₂ derivative, 108°); 4:6-dichloro-2-nitro-*NN*-acetylmethyl-, 60°, -*NN*-nitro-

methyl-, 72°, -*N*-ethyl-, 61°, -*NN*-nitroethyl-aniline, 96°, and the corresponding 4:6- Br_2 -compounds, 89°, —, 74°, and an oil, respectively. The relation between constitution and m.p., colour, and taste of these compounds is discussed. A. L.

Action of magnesium ethyl bromide on butyryl-ethyl-anilide. M. MONTAGNE and Y. ISAMBERT (Compt. rend., 1939, 208, 285—287; cf. A., 1936, 1096).—Butyryl-ethyl-anilide (I) with MgEtBr affords C_2H_5 and $\text{NPhEt}\cdot\text{CO}\cdot\text{CHEt}\cdot\text{MgBr}$, which reacts with COEtPr^a (a by-product) to give, after hydrolysis, β -hydroxy- α - β -diethylhexoethyl-anilide (II). The alternative view that $\text{COPr}\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NPhEt}$ is formed from 2 mols. of (I) and then reacts with MgEtBr is unlikely because (a) it is not found in the reaction product, (b) it is only partly converted into (II) by a large excess of MgEtBr . J. L. D.

Sulphonation of methylaniline. I. S. UPPAL and K. VENKATARAMAN (J.S.C.I., 1938, 57, 410—412).—Proof of the orientation of the three $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (A) is given. Sulphonation of NHPHMe leads to *p*- $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, decomp. 244—246°, or a mixture of this with the *m*-acid, decomp. 286—290°. The *o*-acid, decomp. 220°, is obtained by the methylation (Me_2SO_4) of orthanilic acid. The three isomerides are oriented by an application of Halberkann's method (A., 1921, i, 779), the *p*-toluenesulphonyl derivative of each being prepared by methylation of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ or from (A) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$. The *p*-toluenesulphonyl derivatives are characterised as the arylamine salts; the following are described: $\text{C}_5\text{H}_5\text{N}$, m.p. 255° (very stable to acid hydrolysis), and *p*-chloroaniline, m.p. 230° (decomp.), *p*-toluenesulphonylsulphanilate; benzidine, m.p. 255° (decomp.), *p*-chloroaniline, m.p. 202°, and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 201°, *p*-toluenesulphonyl-*N*-methylsulphanilate; *p*-chloroaniline *p*-toluenesulphonyl-metanilate, m.p. 202°, *p*-toluenesulphonyl-*N*-methyl-metanilate, m.p. 148°, *p*-toluenesulphonylorthanilate, m.p. 214°, and *p*-toluenesulphonyl-*N*-methylorthanilate, m.p. 195° ($\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ salt, m.p. 196°).

Phosphorescence of tetraphenylmethane and related substances. D. B. CLAPP (J. Amer. Chem. Soc., 1939, 61, 523—524).— CPh_4 and 14 of its derivatives, 2-triphenylmethylpyrrole, SiX_4 (X = Ph or *p*- $\text{C}_6\text{H}_4\text{Me}$, but not *p*- $\text{C}_6\text{H}_4\text{Ph}$), SnPh_4 , PbPh_4 (weak), $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, and sucrose fluoresce for various times up to 35 sec. after irradiation with ultra-violet light. Traces of CPh_3 -dyes may be responsible for the effect with CPh_4 derivatives. The time of fluorescence increases as the temp. decreases. $\text{CPh}_3\cdot\text{OH}$, NHPHr (or NPhR_2), and $\text{HCl}\cdot\text{AcOH}\cdot\text{Ae}_2\text{O}$ give 4-ethyl-, m.p. 172—173°, 4-*n*-butyl-, m.p. 135—136°, 4-diethyl-, m.p. 177.5—178.5°, and 4-di-*n*-butyl-aminotetraphenylmethane, m.p. 177—178°.

R. S. C.

Mononitration of α - and β -naphthylamines in presence of carbamide. H. H. HODGSON and W. DAVEY (J.C.S., 1939, 348—349).— $\text{CO}(\text{NH}_2)_2$ and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, dissolved in this order in conc. H_2SO_4 , with KNO_3 (1 mol.) give 8:1- (27%) and 5:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ (43%); 2 mols. give 32.5 and 38%

respectively. Similarly, β -C₁₀H₇NH₂ gives 5.4 and 86.7% or a trace and 70.5% of 8:2- and 5:2-NO₂-C₁₀H₆NH₂, respectively. A. T. P.

Case of simple substitution in the 3-position of a 1:2-disubstituted naphthalene. H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1939, 345—346).—1:2-NO₂-C₁₀H₆NH₂ and Hg(OAc)₂-AcOH give 1-nitro-2-naphthylamine-3-mercuriacetate, converted by I + 10% KI into 3-iodo-1-nitro-2-naphthylamine (I), m.p. 174°, the Ac derivative (by Ac₂O), m.p. 196°, of which is reduced (A., 1936, 718) to the stannichloride of 2:3:1-NHAc-C₁₀H₅I-NH₂. 4:2:1-NO₂-C₁₀H₅I-NH₂ is not similarly acetylated (cf. *loc. cit.*). (I) is deaminated to 3:1-C₁₀H₅I-NO₂. 4:2:1-NO₂-C₁₀H₅Cl-NH₂ affords (diazo-reaction) 1:2-dichloro-4-nitronaphthalene, m.p. 119°, but 2:4:1-NO₂-C₁₀H₅Cl-NH₂ similarly gives only an amorphous product, m.p. 102°. A. T. P.

Carbodi-imide. F. ZETZSCHE and A. FREDRICH (Ber., 1939, 73, [B], 363—365; cf. A., 1938, II, 470).—Carbodi-imides are determined by weighing the CO₂ evolved when they react with H₂C₂O₄ in pure dioxan first at room temp. and finally at 90° (bath). The polymeric β -carboditolyimide reacts similarly to but more slowly than the α - (monomeric) form. H. W.

6:6'-Diamino-4:4'-diisopropylstilbene-2:2'-disulphonic acid.—See B., 1939, 243.

Guanyl- and guanido-naphthalenes. Group migration in cyanonaphthalenes. H. KING and E. V. WRIGHT (J.C.S., 1939, 253—257; cf. A., 1938, III, 63).—K 2-cyanonaphthalene-7-sulphonate (+2.5H₂O) (prep. from 2:7-NH₂-C₁₀H₆SO₃H) or 2:7-C₁₀H₆(SO₃Na)₂, on dry distillation with KCN in CO₂, gives 2:7- (I) and 1:7-C₁₀H₆(CN)₂ (II) (also obtained similarly from 2:8-CN-C₁₀H₆SO₃Na); partial migration of CN thus occurs. Similarly, 2:6-CN-C₁₀H₆SO₃Na and KCN give 2:6- (III) and 1:6-C₁₀H₆(CN)₂ (III) and (I) in dioxan-EtOH, saturated with HCl at 0—5°, and kept at 0° for 14 days, afford imino-ether hydrochlorides, converted by EtOH-NH₃ at 40—50° (under pressure) into 2:6-, m.p. >300°, and 2:7-naphthylenediamidine dihydrochloride, m.p. >290° (+H₂O), respectively. 2:7-C₁₀H₆(NH₂)₂·2HCl refluxed with CN·NH₂ (20 mols.) in EtOH, followed by treatment of the product with aq. NH₄NO₃, gives 7-guanido-2-naphthylamine nitrate, m.p. 251—252°, and 2:7-diguanidonaphthalene dinitrate, m.p. 209°. 1:5-C₁₀H₆(NH₂)₂·2HCl similarly affords 1:5-diguanidonaphthalene dinitrate, m.p. >300°, but 1:8-C₁₀H₆(NH₂)₂·2HCl and CN·NH₂-EtOH give aminoperimidine hydrochloride (+H₂O). 1:5-C₁₀H₆(SO₃Na)₂ and KCN give 1:5-C₁₀H₆(CN)₂, not convertible into the imino-ether. (II) with HCl-EtOH-dioxan, then NH₃-EtOH, gives 1-naphthonitrile-7-amidine hydrochloride, m.p. 296—297° (1-C₁₀H₇-CN derivatives do not give I-amidines). 4:4'-Diaminoazobenzene dihydrochloride and EtOH-CN·NH₂ (30 mols.) followed by NH₄NO₃ afford 4-guanido-4'-aminoazobenzene nitrate, m.p. 257° (decomp.). 4:4'-Dipiperidyl and SMe·C(NH)·NH₂·HI (IV) in aq. NaOH at 80° give an iodide, converted by moist AgCl into 1:1'-di-

guanyl-4:4'-dipiperidyl dihydrochloride (+2H₂O), m.p. 361° (decomp.); monoguanyl-4:4'-dipiperidyl hydriodide, m.p. 136—137° (+H₂O), m.p. 166° (dried at 100°), is isolable from the original mother-liquors. 2:4'-Dipiperidyl and (IV) at 80° give 1'-guanyl-2:4'-dipiperidyl dihydriodide (+H₂O), m.p. ~123°. Tests for trypanocidal action are given; introduction of the C₁₀H₈ nucleus into amidines and guanidines does not impair activity. A. T. P.

Electrochemical oxidation of 5:5'-azo-m-xylene [3:5:3':5'-tetramethylazobenzene]. F. FICHTER and R. GUNST (Helv. Chim. Acta, 1939, 22, 267—275).—3:5:3':5'-Tetramethylazobenzene, m.p. 136—137° (prep. by electrochemical reduction of 1:3:5-C₆H₃Me₂·NO₂ described), is dissolved in 90% H₂SO₄ and oxidised at a Pt anode giving unchanged material, 2:6-dimethyl-p-benzoquinone, m.p. 71°, and an ill-defined oxidation product (I) transformed by Ac₂O in C₅H₅N into 4:4'-diacetoxy-3:3':5:5'-tetramethylazobenzene (II), decomp. ~300° (softens at 110—130°). Diazotisation of *vic*-m-xylidine in presence of KNO₃ leads to 4:2:6:1-NO₂-C₆H₂Me₂·OH. Electrochemical reduction of the corresponding acetate, m.p. 112°, appears to give the corresponding azobenzene but the process is accompanied by some loss of Ac and the product is therefore reduced and then acetylated to 5-acetamido-2-acetoxy-m-xylene, m.p. 157°, more conveniently obtained by treatment of 4:2:6:1-NO-C₆H₂Me₂·OH, m.p. 165° (decomp.), with (NH₄)₂S and subsequent acetylation. This is also obtained by reductive fission and subsequent acetylation of (II), whereby the structure of (I) is established. 5-Benzamido-m-2-xylénol, m.p. 188° [benzoate, m.p. 196°, obtained by reductive fission followed by benzoylation of (I)], is described. Chromatographic purification of (I) by Al₂O₃ leads to homogeneous 4:4'-dihydroxy-3:5:3':5'-tetramethylazobenzene, decomp. >160°. 5-Nitroso-m-2-xylénol Me ether, m.p. 51°, from the phenol and CH₂N₂, suffers partial loss of Me when reduced; the product is diazotised and coupled with *vic*-m-xylénol to a compound, C₁₇H₁₀O₂N₂ or C₁₆H₁₈O₂N₂, decomp. 199°, which is converted by Me₂SO₄ and alkali into 4:4'-dimethoxy-3:5:3':5'-tetramethylazobenzene, m.p. 139°.

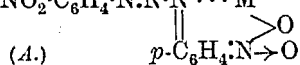
H. W.

Homologous series of acylated azo-dyes from o- and p-acylamidophenols and 1:7-acylamidonaphthols. H. E. FIERZ-DAVID and W. KUSTER (Helv. Chim. Acta, 1939, 22, 82—112).—The most marked influence on the surface tension of aq. solutions of acylated azo-dyes and on alkaline solutions of acylated amino-phenols and -naphthols is exerted by the decao to palmitic residues. Higher fatty acids with an odd no. of C are usually obtained from the requisite alkyl halide through the corresponding nitriles. Et palmitate is converted by MgPhBr into diphenylpentadecylcarbinol, m.p. 46°, dehydrated at 220—260° to α -diphenyl- β -tetradecylethylene, m.p. 18—20°, which is oxidised (CrO₃ in AcOH) to pentadecic acid, m.p. 51°. α -Bromostearic acid is converted by aq. KOH into α -hydroxystearic acid, which at 250—280° passes into margaraldehyde, oxidised (KMnO₄ in COMe₂) to margaric acid. The

acids are converted into their chlorides by SOCl_2 . Acylation of *o*- and *p*-aminophenols is effected by treating the base dissolved as salt of the requisite acid in H_2O with the anhydride of the same acid, by the use of the acid chloride [when necessary in presence of an acid-absorbent ($\text{C}_5\text{H}_5\text{N}$, NaOAc , CaCO_3)], or by melting the phenol and acid together. The following are described: *o*-form-, m.p. 130°, -acet-, m.p. 207°, -propion-, m.p. 78°, -butyr-, m.p. 81°, -valer-, m.p. 82°, -hexo-, m.p. 74°, -hepto-, m.p. 83°, -octo-, m.p. 71°, -nono-, m.p. 86°, -deco-, m.p. 72°, -laur-, m.p. 69°, -myrist-, m.p. 70°, -palmit-, m.p. 77°, and -stear-, m.p. 82°, -amidophenols; *p*-form-, m.p. 139°, -acet-, m.p. 169°, -propion-, m.p. 173°, -butyr-, m.p. 138°, -valer-, m.p. 101°, -hexo-, m.p. 112°, -hepto-, m.p. 114°, -octo-, m.p. 123°, -nono-, m.p. 124°, -deco-, m.p. 130·5°, -laur-, m.p. 131°, -myrist-, m.p. 133·5°, -palmit-, m.p. 134·5°, and -stear-, m.p. 135·5°, -amidophenols; *o*-ON-dibutyl-, m.p. 76°, -divaleryl-, m.p. 71—73°, -diheptoyl-, m.p. 47°, -dioctoyl-, m.p. 57°, -dinonoyl-, m.p. 59°, -didecoyl-, m.p. 62°, -dilauryl-, m.p. 65°, -dimyristyl-, m.p. 65°, and -distearyl-, m.p. 62°, -aminophenols; *p*-ON-divaleryl-, m.p. 114°, -diheptoyl-, m.p. 118—120°, -diheptoyl-, m.p. 119·5°, -dioctoyl-, m.p. 127—128°, -dinonoyl-, m.p. 124°, -didecoyl-, m.p. 130°, and -dilauryl-, m.p. 119—120°, -aminophenols. *o*-NN-Distearamidophenol, m.p. 92°, pentadecylbenzoxazole, m.p. 45·5°, and heptadecylbenzoxazole, m.p. 55°, are described incidentally. The following *N*-acyl derivatives of 1:7- $\text{NH}_2\text{C}_{10}\text{H}_6\text{OH}$ are described: *form*-, m.p. 204°; *acet*-, m.p. 198° (decomp.); *propion*-, m.p. 138°; *butyr*-, m.p. 161°; *valer*-, m.p. 171°; *hexo*-, m.p. 156°; *hepto*-, m.p. 147°; *octo*-, m.p. 139°; *nono*-, m.p. 137°; *deco*-, m.p. 131°; *undeco*-, m.p. 127°; *laur*-, m.p. 125°; *trideco*-, m.p. 127°; *myrist*-, m.p. 126°; *pentadeco*-, m.p. 128°; *palmit*-, m.p. 129°; *heptadeco*-, m.p. 129°; *stear*-, m.p. 130°; *nonadeco*-, m.p. 129°; *ole*-, m.p. 122°; *benz*-, m.p. 211°. The following diacyl derivatives of 1:7- $\text{NH}_2\text{C}_{10}\text{H}_6\text{OH}$ are described: *diacetyl*-, m.p. 177°; *dibutyl*-, m.p. 103°; *divaleryl*-, m.p. 77°; *diheptoyl*-, m.p. 87°; *ditriceoyl*-, m.p. 87°; (?) *distearyl*-, m.p. 102°; *dibenzoyl*-, m.p. 208° (all m.p. are corr.). The coupling of acylated *o*- and *p*-aminophenols with diazotised *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ proceeds relatively smoothly with the lower homologues only; the *p*-compounds are particularly unsuitable. EtOH, when used as solvent, is partly oxidised to MeCHO. In most cases considerable amounts of unchanged base remain after disappearance of the diazo-reaction. Acylated 1:7-aminonaphthols couple readily. The compounds derived from *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ are usually too sparingly sol. for physiological purposes. The following Na_2 2'-hydroxy-8'-acylamido-1'-naphthaleneazobenzene-2:5-disulphonates have therefore been prepared, usually retaining a certain proportion of NaCl: -*form*-, -*acet*-, -*propion*-, -*butyr*-, -*valer*-, -*hexo*-, -*hepto*-, -*octo*-, -*nono*-, -*deco*-, -*undeco*-, -*laur*-, -*trideco*-, -*myrist*-, -*pentadeco*-, -*palmit*-, -*heptadeco*-, -*stear*-, -*nonadeco*-, -*ole*-, -*benz*-. H. W.

Reactions and salts of 4:4'-dinitrodiazoaminobenzene. F. P. DWYER (J.S.C.I., 1939, 58, 110—116).—The dark violet Na, K, and Ba salts, BaR_2 ,

($\text{R} = \text{C}_{12}\text{H}_8\text{O}_4\text{N}_5$), of 4:4'-dinitrodiazoaminobenzene (I) are considered to have the *aci*-structure (A) (cf. A., 1938, II, 483); they are readily sol. in EtOH, $\text{p-NO}_2\text{C}_6\text{H}_4\text{N:N}\cdots\text{M}$ COMe₂, PhNO₂, and hot aq. alkali, and are hydrolysed by hot H_2O . Alkali-metal salts of



the triazen form appear to be incapable of existence. The yellow $\text{C}_5\text{H}_5\text{N}$ salt, $\text{NAr:N:NArH}\cdot\text{C}_5\text{H}_5\text{N}$ ($\text{Ar} = \text{p-NO}_2\text{C}_6\text{H}_4$), obtained when a solution of either form (*loc. cit.*) of (I) in hot, dry $\text{C}_5\text{H}_5\text{N}$ is cooled, undergoes tautomeric change in presence of H_2O , MeOH, EtOH, or COMe₂ (decreasing intensity in the order quoted) to the *aci*-salt (purplish-red; not isolable), which is stabilised by co-ordination, e.g., $\text{N} \rightarrow \text{H}\cdot\text{OH}$. The NH_4 salt resembles the $\text{C}_5\text{H}_5\text{N}$ salt. (I) (in COMe₂) with $\text{MeOH-C}_5\text{H}_5\text{N-AgNO}_3 + \text{NaOAc}$ gives the

yellow Ag salt, $\text{Ag} \begin{array}{c} \text{NAr} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$, converted by $\text{C}_5\text{H}_5\text{N}$ at

100° into the purple salt (II), $\text{AgR}\cdot\text{C}_5\text{H}_5\text{N}$ (A with $\text{M} = \text{Ag}\leftarrow\text{C}_5\text{H}_5\text{N}$), which when heated alone or with EtOH or COMe₂ regenerates the yellow salt. Meldola's Ag salt (J.C.S., 1887, 50, 446) is undoubtedly the *amine*, $\text{AgR}\cdot\text{NH}_3$. Treatment of the product obtained from (I) and $\text{Cu}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}$ in EtOH-COMe₂-3N-NaOAc with $\text{C}_5\text{H}_5\text{N}$ gives the violet salt, $\text{CuR}\cdot\text{C}_5\text{H}_5\text{N}$, which is converted by heating to 100° or by warm EtOH or COMe₂ into the orange-yellow normal salt, CuR . This with dry NH_3 in C_6H_6 affords the *amine*, $\text{CuR}\cdot\text{NH}_3$, and with aq. EtOH-CS(NH_2)₂ gives the black compound, $\text{CuR}\cdot 3\text{CS}(\text{NH}_2)_2$. Since one $\text{C}_5\text{H}_5\text{N}$ or NH_3 is co-ordinated in the above Ag and Cu salts, it is deduced that (I) (*aci*-form) supplies one co-ordination position. Attempts to prepare a Me derivative of the *aci*-form of (I) from (II) and MeI-moist Ag_2O yielded only the usual yellow, triazen derivative; the Me cannot act as acceptor to the donor azo-N. The Cu^{++} salt, $\text{CuR}_2\cdot 2\text{C}_5\text{H}_5\text{N}$, blue, and Hg^{++} salt, $\text{HgR}_2\cdot 2\text{C}_5\text{H}_5\text{N}$, orange-red, are co-ordinated normal salts dissolving in $\text{C}_5\text{H}_5\text{N}$ to orange solutions; removal of $\text{C}_5\text{H}_5\text{N}$ from the former gives the Cu⁺ salts. Attempts to prepare the unco-ordinated Cu^{++} salt were unsuccessful; a salt, probably $\text{CuR}(\text{C}_{12}\text{H}_8\text{O}_4\text{N}_5)_2$, was obtained with other products from the Na salt of (I) and $\text{MeOH-CuCl}_2\cdot 2\text{H}_2\text{O}$. The normal and *aci*-forms of (I) with conc. HCl at 100° (bath) give N₂, *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$, and 43 and 62% respectively of $\text{p-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$. H. B.

Triaryl phosphates.—See B., 1939, 244.

Detoxication of ingested naphthalene.—See A., 1939, III, 302.

Synthesis of phenanthrenes. A. SCHÖNBERG and F. L. WARREN (Chem. and Ind., 1939, 199).—Synthesis of 9-hydroxyphenanthrene from *o*- $\text{C}_6\text{H}_4\text{Ph-COCl}$ by way of *o*-diazo-*o*-phenylacetophenone (prep. by CH_2N_2), m.p. 106°, and *o*-diphenylacetic acid (prep. by colloidal Ag in H_2O), m.p. 116°, is announced without details. R. S. C.

Oxidation of phenol by hydrogen peroxide in presence of ferrous sulphate. A. CHWALA and M. PAILER (J. pr. Chem., 1939, [ii], 152, 45—48).—

Repetition of the work of Goldhammer (A., 1927, 1181) shows that considerable amounts of quinol (I) and some more highly oxidised material are formed in addition to α -C₆H₄(OH)₂ (II). Under defined conditions the yield of (I) + (II) is almost 72% of the PhOH taken. It appears essential that PhOH should be in excess with respect to H₂O₂ and also to (I) + (II), and that PhOH and H₂O₂ are in very dil. solution. p_H 3–4 is most suitable. H. W.

Synthesis and bactericidal properties of 5-n-alkylresorcinols. C. M. SUTER and A. W. WESTON (J. Amer. Chem. Soc., 1939, 61, 232–236).—1 : 3 : 5-C₆H₃Br₃ does not give Mg or Li derivatives. Indirect prep. of 3 : 5 : 1-C₆H₃Br₂Alk was not practicable. 3 : 5 : 1-(OMe)₂C₆H₃·CO·NH₂ and MgAlkHal give slowly 80–88% of 3 : 5-dimethoxyphenyl Pr^a, b.p. 157–158°/7 mm., m.p. 33·5–34° (semicarbazone, m.p. 188°), Et, b.p. 162–163°/11 mm., m.p. 32·5° (semicarbazone, new m.p. 131·5–132°), Bu^a, n-amyl, b.p. 175–176°/7 mm., m.p. 53° (semicarbazone, m.p. 183–184°), and n-hexyl ketone, b.p. 161–161·5°/3 mm., m.p. 30·5–31° (semicarbazone, m.p. 133·5–134°). The appropriate hydrazones with KOH at 200–245° give 3 : 5-dimethoxy-n-butyl-, b.p. 125–128°/6 mm., -n-propyl-, b.p. 103–105°/3 mm., -n-amyl-, b.p. 133–136°/6 mm., -n-heptyl-, b.p. 162–163°/6 mm., and -n-hexyl-benzene, b.p. 141–143°/7 mm. [with considerable amounts of azine]. Demethylation then gives 5-n-propyl-, b.p. 148–149°/3 mm., new m.p. 86·5–86·7°, and +H₂O, new m.p. 47° (Br₃-derivative, m.p. 97·5–98°), 5-n-amyl-, b.p. 162–164°/5 mm. (Br₃-derivative, m.p. 85°), 5-n-heptyl-, b.p. 179–181°/6 mm., new m.p. 55–55·5° (Br₃-derivative, m.p. 73·5–74·5°), 5-n-butyl-, b.p. 151–152°/3 mm., m.p. 81·5–82·5° (Br₃-derivative, m.p. 84–84·5°), and 5-n-hexyl-resorcinol, b.p. 192–195°/11 mm., m.p. (+H₂O) 49–49·5° (Br₃-derivative, m.p. 75–76°), which have PhOH coeff. 5, 35, 128, 10, and 49, respectively, against *S. aureus*. Hydrogenation (Pd) of the ketones is very slow. 3 : 5-Dimethoxybenzdiethylamide, b.p. 166·5–167°/3·5 mm., with MgAlkHal gives very little ketone. 3 : 5-(OMe)₂C₆H₃·COCl with CdBu^a₂ gives only 27% of ketone and with ZnAlk₂ gives mostly the ester. 3 : 5-Dimethoxyphenyl Pr^a ketazine has m.p. 96·5–97°. The KBr–KBrO₃ titration of resorcinols is improved. R. S. C.

Oxidation processes. XIII. Inhibitory action of sulphite and other compounds in the autoxidation of quinol and its homologues. T. H. JAMES and A. WEISSBERGER (J. Amer. Chem. Soc., 1939, 61, 442–450; cf. A., 1938, II, 440).—By suitably adjusting p_H and adding sp. inhibitors for the oxidation of Na₂SO₃, and owing to quinones etc. inhibiting the oxidation of Na₂SO₃, the rate of oxidation of quinols in presence of an excess of Na₂SO₃ is measured. The complex results are explained by assuming oxidation of quinols to quinones and H₂O₂, oxidation of Na₂SO₃ by H₂O₂, and interaction of quinones with Na₂SO₃ to form quinolmonosulphonates (followed by oxidation to quinonesulphonates and, if H is still available, further reaction thereof with Na₂SO₃ etc.). Cysteine, SH·CH₂·CO₂H, SH·CH₂·CO·NHPh, and p-C₆H₄Me·SH inhibit oxidation of quinol by forming compounds

with the catalytic p-O·C₆H₄·O formed; these compounds later oxidise faster than does p-O·C₆H₄·O. R. S. C.

Mechanism of the autoxidation of ψ -cumoquinol. G. KORNFIELD and A. WEISSBERGER (J. Amer. Chem. Soc., 1939, 61, 360–363).—Previous quant. results (A., 1938, II, 440) are explained on the assumptions that reaction of ψ -cumoquinol (I) with O₂ involves reaction of the intermediate semiquinone with (a) O₂ and (b) ψ -cumoinone (II) to yield a complex (analogous to verdoflavin), which then decomposes into (I) and (II). R. S. C.

Condensation of ketones with phenols. M. E. MCGREAL, V. NIEDERL, and J. B. NIEDERL (J. Amer. Chem. Soc., 1939, 61, 345–348).—PhOH, COR₂, and HCl in AcOH give CR₂(C₆H₄·OH·p)₂ (by way of p-OH·C₆H₄·CR₂·OH), converted by distillation/1 atm. into PhOH, p-OH·C₆H₄·CHR₂, and tar. Thus are obtained $\beta\beta$ -di-p-hydroxyphenyl-, m.p. 125° [(NO₂)₄-derivative, m.p. 168°], and -di-6-hydroxy-m-tolylbutane, m.p. 146° (diacetate, m.p. 71°), $\beta\beta$ -di-p-hydroxyphenyl-pentane, m.p. 149°, and -8-methylpentane, m.p. 150° [(NO₂)₄-derivative, m.p. 154°], $\beta\beta$ -di-6-hydroxy-m-tolyl-8-methylpentane, m.p. 129°, 1 : 1-di-p-hydroxyphenyl-, m.p. 184° (diacetate, m.p. 124°; bisphenylurethane, m.p. 148°), and 1 : 1-di-6'-hydroxy-m-tolyl-cyclohexane, m.p. 186° (derived di-O-acetic acid, m.p. 232°; bisphenylurethane, m.p. 142°), 1 : 1-di-p-hydroxyphenyl-3-methylcyclohexane, m.p. 167°, -4-methylcyclohexane, m.p. 180°, and -cyclopentane, m.p. 156°, p-hydroxyphenyl-cyclohexane, m.p. 132° (derived aryl-oxyacetic acid, m.p. 145°), -3-methylcyclohexane, m.p. 110° (derived aryl-oxyacetic acid, m.p. 127°), -4-methylcyclohexane, m.p. 118° (derived aryl-oxyacetic acid, m.p. 136°), and -cyclopentane, m.p. 90° (derived aryl-oxyacetic acid, m.p. 115°), 6'-hydroxy-m-tolylcyclohexane, m.p. 126° (derived aryl-oxyacetic acid, m.p. 134°), α -phenyl-, m.p. 175° (diacetate, m.p. 180°), and α -p-tolyl- α -di-p-hydroxyphenylethane, m.p. 133° (diacetate, m.p. 151°), and α -phenyl- α -di-6-hydroxy-m-tolylethane, m.p. 141° (diacetate, m.p. 118°). R. S. C.

Oxidation of 1 : 8-dihydroxynaphthalene and its monomethyl ether with peracetic acid. J. BÖSEKEN and L. G. SMITT (Rec. trav. chim., 1939, 58, 125–131; cf. A., 1935, 614).—With AcO₂H (1–1·2 mols.) in AcOH, 1 : 8-C₁₀H₆(OH)₂ gives only resinous products, but its Me₁ ether (CH₂N₂), m.p. 47°, yields 8-methoxy- α -naphthaquinone, m.p. 184°, and (?) 7-methoxyindenone-2-carboxylic acid, m.p. 200°, formed by dehydration of 2-carboxy-3-methoxyall-cinnamic acid. 8 : 1-NHAc·C₁₀H₆·OH when distilled at 16 mm. yields 2-methylperinaphthoxazine, m.p. 72°, which reverts to the former when cryst. from EtOH. A. Li.

Aromatic fluoro-compounds. M. SEYHAN [with N. ESMEK] (Ber., 1939, 72, [B], 365–366; cf. Schiemann and Seyhan, A., 1938, II, 52).—Improved methods are described for the conversion of 4 : 2 : 1-NO₂·C₆H₃F·OEt into 4 : 2 : 1-NH₂·C₆H₃F·OEt and thence into 3-fluoro-4-ethoxybenzenediazonium borofluoride, decomp. 82°, and 2 : 4-difluorophenetole, b.p. 72°/18 mm. H. W.

Pyrolysis of cyclohexenyl phenyl ether. J. W. CORNFORTH, G. K. HUGHES, and F. LIONS (J. Proc.

Roy. Soc. New South Wales, 1938, **71**, 323—329).—1:2-Dibromocyclohexane is transformed by NaOPh in boiling EtOH into Δ^2 -cyclohexenyl Ph ether (I), b.p. 135°/21 mm., hexahydrodiphenylene oxide (II), b.p. 157—159°/22 mm., a product, b.p. 220—222°/22 mm., and o-cyclohexenylphenol (III), b.p. 153—154°/22 mm.; on one occasion a product, $C_{12}H_{14}O$, m.p. 68° with softening, was isolated from the Et_2O extract of the phenols which contained HCl. The structure of (I) is established by its formation from 1-bromo- Δ^2 -cyclohexene, PhOH, and anhyd. K_2CO_3 in boiling $COMe_2$. It is oxidised to α -phenoxyadipic acid, m.p. 142°. At 215° (I) passes mainly into (II) with a smaller proportion of (III). Dehydrogenation of (II) by Se at 290—300° yields diphenylene oxide, characterised as the 3:6- Br_2 -derivative. (III) is characterised by conversion into o-cyclohexenylphenoxycetic acid, m.p. 143—144°, and by methylation (Me_2SO_4 -NaOH) to o-cyclohexenylanisole, b.p. 150—151°/22 mm., oxidised to α -o-anisyladipic acid, m.p. 179—180°. H. W.

Alkoxyalkyl derivatives of resorcinol. C. D. HURD and G. W. FOWLER (J. Amer. Chem. Soc., 1939, **61**, 249—254).—Resorcinol alkoxyalkyl monoethers are less efficient bactericides than are the corresponding alkyl ethers. $OEt \cdot [CH_2]_2 \cdot Cl$ and di-(β -ethoxyethyl) sulphite (prep. from the alcohol and $SOCl_2$), b.p. 120°/5 mm., do not react with $m\text{-OH} \cdot C_6H_4 \cdot ONa$ (I), but the appropriate bromides in aq. $COMe_2$ give resorcinol β -ethoxyethyl, b.p. 146—152°/3 mm., β -butoxyethyl, b.p. 153—160°/2 mm., γ -ethoxypropyl, b.p. 165—170°/4 mm., m.p. 38—39°, and γ -butoxypropyl monoether, b.p. 170—172°/2 mm., with smaller amounts of the di(alkoxyalkyl) ethers, b.p. 170—175°/4 mm., 181—185°/2 mm., 171—180°/4 mm., and 181—189°/2 mm., respectively. γ -Butoxypropyl bromide has b.p. 80—83°/21 mm. ($CH \cdot CH_2 \cdot Br$)₂ (prep. from butadiene described), m.p. 50—52°, and NaOMe give δ -methoxycrotyl bromide, b.p. 54.5—56.5°/10 mm., which with (I) in $C_6H_5 \cdot N_2$ gives (?) impure 4-methoxycrotylresorcinol (polymerised on "mol." distillation) and thence 2:4-di(carboxymethoxy)-1- δ -methoxycrotylbenzene, m.p. 148—150°, and (H_2 -Pd) impure (?) 4- δ -methoxybutylresorcinol. Most methods of preparing 2:4:1-(OH)₂ C_6H_3 ·CO·CH₂·Oalk failed, but the Hoesch synthesis yields ω -butoxy- (II), m.p. 64—65°, and ω -propoxy-resacetophenone, m.p. 106—107°; $OEt \cdot [CH_2]_2 \cdot CN$ similarly gives 2:4:1-(OH)₂ C_6H_3 ·[CH₂]₂·CO₂H. Clemmensen reduction converts (II) into 4:1:1:3- $C_6H_3Et(OH)_2$ (derived di-O-acetic acid, m.p. 180—181°), also formed from resacetophenone and H_2 -Pd (poor yield). $CH_2Cl \cdot OBu$ and CuCN at 100° give 77.3% of butoxyacetoneitrile, b.p. 167—171°/738 mm. ω -Methoxyresacetophenone oxime has m.p. 158°. R. S. C.

Polymerisation of ethylchavicol. $\alpha\zeta$ -Di-p-ethoxyphenyl- Δ^2 -hexene. J. M. VAN DER ZANDEN (Rec. trav. chim., 1939, **58**, 181—192; cf. A., 1938, II, 181).—Ethylchavicol heated at 250° for 250 hr. yields $\alpha\zeta$ -di-p-ethoxyphenyl- Δ^2 -hexene (I), m.p. 101—101.5° (dibromide, m.p. 96—96.5°), a trimeride, m.p. 119.5—120°, and a small amount of $p\text{-OEt} \cdot C_6H_4 \cdot CH \cdot CHMe$. In presence of Mg a third polymeride is obtained. The constitution of (I) is

shown by oxidation ($KMnO_4$ in $COMe_2$) to $p\text{-OEt} \cdot C_6H_4 \cdot CO_2H$ and δ -p-ethoxyphenyl-n-valeric acid (II), m.p. 104.5—105°, synthesised as follows: γ -p-ethoxyphenylpropyl alcohol, m.p. 49.3—49.6° (prep. according to the scheme: $p\text{-OEt} \cdot C_6H_4 \cdot CHO + EtOAc \rightarrow p\text{-OEt} \cdot C_6H_4 \cdot CH \cdot CH \cdot CO_2Et \rightarrow p\text{-OEt} \cdot C_6H_4 \cdot [CH_2]_3 \cdot OH$), yields a bromide, b.p. 156—158°/14 mm., which with $CH_2(CO_2Et)_2$ and $EtOH$ -NaOEt gives the Et ester, b.p. 190—195°/2 mm., of δ -p-ethoxyphenylbutane- $\alpha\alpha$ -dicarboxylic acid, m.p. 113—115°, which yields (II) when heated at 130°/vac. Oxidation (CrO_3) of (II) affords γ -p-ethoxybenzoylbutyric acid, m.p. 116.5—117° (p-nitrophenyl-, m.p. 168—168.5°, and 2:4-dinitrophenyl-hydrazone, m.p. 141.8—142.2°) [further oxidised ($KMnO_4$) to $p\text{-OEt} \cdot C_6H_4 \cdot CO_2H$ and $p\text{-OEt} \cdot C_6H_4 \cdot CO \cdot CO_2H$], the oxime, m.p. 115—115.5°, of which with PCl_5 in cold Et_2O yields N-p-ethoxyphenylglutarimide, m.p. 156.5—157° (synthesised from $p\text{-OEt} \cdot C_6H_4 \cdot NH_2$ and $CO_2H \cdot [CH_2]_3 \cdot CO_2H$), hydrolysed (aq. $EtOH$ -NaOH) to N-p-ethoxyphenylglutaramic acid, m.p. 134.5—135°, and thence (conc. HCl) to $CO_2H \cdot [CH_2]_3 \cdot CO_2H$ and $p\text{-OEt} \cdot C_6H_4 \cdot NH_2$. (I) is reduced (Pt) to $\alpha\zeta$ -di-p-ethoxyphenylhexane, m.p. 68.5—69°, also prepared from $p\text{-OEt} \cdot C_6H_4 \cdot [CH_2]_3 \cdot Br$ and Na in Et_2O . A. Li.

Nitration of 2-methoxydiphenyl ether. F. LIONS and A. M. WILLISON (J. Proc. Roy. Soc. New South Wales, 1938, **71**, 435—448).—2-Methoxydiphenyl ether, m.p. 78°, is converted by HNO_3 (d 1.42) in AcOH at $\geq 40^\circ$ into 5- (I), m.p. 69°, and 4- (II), b.p. 190—191.5°/1.7 mm., 175°/0.8 mm., -nitro-2-methoxydiphenyl ether. (I) is slowly hydrolysed by boiling aq. KOH to 5-nitro-2-hydroxydiphenyl ether, m.p. 63° (Ac derivative, m.p. 108°). The synthesis of (I) is recorded from the K salt of 5-nitroguaiacol, boiling PhBr, and Cu powder and from 2-bromo-4-nitroanisole, KOPh, and Cu powder at 180—200°. (II) is obtained synthetically from 2-iodo-5-nitroanisole (III), KOPh, and Cu powder at 180—200°. (III) and boiling piperidine give 4-nitro-2-methoxy-1-piperidinobenzene, m.p. 76°. (I) is reduced by Na_2S in aq. EtOH to 5-amino-2-methoxydiphenyl ether, m.p. 79° [hydrochloride, m.p. 234°; Ac (IV), m.p. 115°, formyl, m.p. 120°, p-, m.p. 87°, and o-, m.p. 112°, -nitrobenzylidene derivatives]. HNO_3 (d 1.42) converts (IV) in AcOH at $\geq 25^\circ$ into 4-nitro-5-acetamido-2-methoxydiphenyl ether, m.p. 141°; reduced ($SnCl_2$ and Sn in boiling glacial AcOH) to 5-phenoxy-6-methoxy-2-methylbenzimidazole, m.p. 149° (also + C_6H_6 of crystallisation), and hydrolysed by acid to 4-nitro-5-amino-2-methoxydiphenyl ether (V), m.p. 167°. Similarly, (II) is reduced to 4-amino-2-methoxydiphenyl ether, m.p. 119°. The corresponding Ac derivative, m.p. 138°, is transformed by HNO_3 (d 1.42) in glacial AcOH at room temp. into 5-nitro-4-acetamido-2-methoxydiphenyl ether, m.p. 124°, hydrolysed to 5-nitro-4-amino-2-methoxydiphenyl ether (VI), m.p. 158°. Gradual addition of Zn dust to (V) or (VI) in EtOH containing conc. HCl followed by phenanthraquinone in aq. $NaHSO_3$ gives 3-phenoxy-2-methoxyphenanthraquinone, m.p. 270°. Trinitro-2-methoxydiphenyl ether has m.p. 204°. H. W.

Free radicals and radical stability. III. 3:4-Methylenedioxytriphenylmethyl and phenyl-p-

anisylldiphenylmethyl. S. T. BOWDEN, W. E. HARRIS, and D. I. ROBERTS (J.C.S., 1939, 302—307; cf. A., 1939, II, 110).—Me piperonylate and MgPhBr give 3 : 4-methylenedioxytriphenyl-carbinol, m.p. 105° (pink solution in liquid SO₂), reduced by Zn-AcOH to the -methane, m.p. 65°, or converted by AcCl in Et₂O-light petroleum, in absence of H₂O, into 3 : 4-methylenedioxytriphenylmethyl chloride (I), m.p. 105° [1 : 1 adducts with FeCl₃, m.p. 145—146°, ZnCl₂ (hygroscopic), HgCl₂, and SnCl₄]. The corresponding bromide has m.p. 121° (HgBr₂ adduct, hygroscopic). (I) and excess of Hg in Et₂O in absence of air give an orange-red solution; air oxidation then gives the peroxide (II), m.p. 173° (from C₆H₆ in atm. of CO₂), in somewhat greater yield than (CPh₃·O)₂ is obtained (*loc. cit.*). The free radical (III) (from the above halides in PhBr with Ag or Hg) absorbs O₂ (method : *loc. cit.*), with further slow oxidation of (II). (III) [from (I) in C₆H₆-Ag in absence of O₂ and light] absorbs I at room temp. and the thermal stability of the iodide is < that of CPh₃I. Isolation of the radical from C₆H₆ solution (method : *loc. cit.*) gives crystals, m.p. 156° (vac.), which in Et₂O with air give (II). Radical photodecomp. in sunlight is less rapid than with CPh₃ (cf. A., 1928, 747). The thermodynamic stability of 3 : 4-methylenedioxytriphenylmethyl is slightly < that of the 3 : 4-(OMe)₂-analogue. *p*-C₆H₄Ph·MgBr and *p*-OMe·C₆H₄·COPh give a product, hydrolysed by H₂SO₄-ice to phenyl-*p*-anisylldiphenyl-carbinol (IV), m.p. 78° (solution in liquid SO₂ is reddish-orange; halochromic salts with strong acids; the corresponding -methane has m.p. 92°). Its basicity is 9.6 compared with 1.7 for diphenyl-*p*-diphenyl-carbinol, new m.p. 106° (cf. Schlenk *et al.*, A., 1909, i, 791), and 1.0 for CPh₃·OH. (IV) and AcCl give the chloride (not cryst.) (*ferrichloride*; *mercurichloride*), which with mol. Ag in Et₂O in the dark gives a deep wine-red solution of the free radical (not isolated) (*peroxide*, m.p. 166°). It is inferred that radical stability is > that of diphenyldiphenylmethyl. The rate of decomp. of phenyl-*p*-anisylldiphenylmethyl formate at 99° is slightly > that of diphenyldiphenylmethyl formate in early stages of reaction. A. T. P.

Derivatives of 9 : 10-dihydroanthracene. J. N. GRAVES, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 318—322).—3 : 4 : 3' : 4'-Tetramethoxydiphenylmethane (I) could not be condensed with PhCHO in presence of ZnCl₂ (under varied conditions) or boiling, conc. HCl; AlCl₃ causes demethylation with much charring. (I) does not condense with CHPhCl₂ in CS₂ containing AlCl₃. Veratrole is transformed by CHPhCl₂ and AlCl₃ in CS₂ into 3 : 4 : 3' : 4'-tetramethoxytriphenylmethane (II), m.p. 124°, and 2 : 3 : 6 : 7-tetramethoxy-9 : 10-diphenyl-9 : 10-dihydroanthracene, m.p. 308°. HNO₃ (d 1.42) in AcOH at 100° converts (II) into a (NO₂)₂-derivative, m.p. 204°, which could not be reduced to the corresponding diamine. H. W.

Reaction of sulphur with halogenated derivatives of diphenyl sulphide. J. H. BILLMAN and G. DOUGHERTY (J. Amer. Chem. Soc., 1939, 61, 387—389).—With S at 240—270° (*p*-C₆H₄Br)₂S (I) gives *p*-C₆H₄Br₂ (II), (*p*-C₆H₄Cl)₂S gives *p*-C₆H₄Cl₂, *p*-C₆H₄Br·SPh gives (II) (trace) and PhBr, *p*-C₆H₄Cl·SPh

gives PhCl, and *p*-C₆H₄Cl·S·C₆H₄Br·*p* gives (II) and *p*-C₆H₄ClBr. In all cases complex sulphides and polysulphides are also formed. The reaction mechanism is : (I) + *x*S → *p*-C₆H₄Br·S·C₆H₄·[S]_{*x*}·Br (III); (III) + (I) → *p*-C₆H₄Br·S·C₆H₄·[S]_{*x*}·SBr(C₆H₄Br·*p*)₂ → (II) + *p*-C₆H₄Br·S·C₆H₄·[S]_{*x*+1}·C₆H₄Br·*p*, etc. R. S. C.

Synthesis of *p*-methylbenzyl acetate from toluene. P. P. SCHORIGIN and A. V. BOGDANOVA (J. Appl. Chem. Russ., 1938, 11, 1217—1221).—A mixture of PhMe, 35% aq. CH₂O, and ZnCl₂ is saturated with HCl (4 hr. at 35°, then 4 hr. at 75°), to give *p*-C₆H₄Me·CH₂Cl, which with KOH-EtOH yields *p*-methylbenzyl Et ether, b.p. 75°/6 mm., hydrolysed by boiling 6% NaHCO₃ to *p*-C₆H₄Me·CH₂·OH. This with Ac₂O-H₃PO₄ or AcOH-H₂SO₄ at room temp. yields the acetate. R. T.

Phenylethyl thioacetate. B. HOLMBERG (Arkiv Kemi, Min., Geol., 1938, 12, B, No. 47, 3 pp.).—Interaction of styrene and AcSH yields β-phenylethyl thioacetate (I), b.p. 134—135°/13 mm., also formed from CH₂Ph·CH₂·SH (II) and AcCl in C₅H₅N. With Br in aq. AcOH (I) yields CH₂Ph·CH₂·SO₂Br, with aq. EtOH-NaOH gives (II), and with H₂O₂, di-β-phenylethyl disulphoxide and CH₂Ph·CH₂·SO₂H are produced. Interaction of CHPhMe·SH and AcCl in C₅H₅N yields α-phenylethyl thioacetate, b.p. 123—125°/13 mm. J. D. R.

Walden inversion. XXI. Halogenation of aromatic carbinols. Rotatory dispersion of aromatic carbinols and corresponding bromides. P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1939, 127, 237—249; cf. A., 1938, II, 360).—In the action of HBr on CHPhR·OH the halide can be formed by at least three different mechanisms, their relative importance depending on the temp. For R = Me, Et, or Prⁿ the *l*-carbinol reacts chiefly without inversion between -80° and -36° through the formation of an additive compound with HBr. Evidence is recorded to show that the reaction in which the configuration is retained proceeds also by a second mechanism, a third being responsible for the reaction in which, at higher temp., inversion occurs (cf. Hughes *et al.*, A., 1937, II, 363). Racemisation of the bromides does not occur below 0°, and the smallness of the rotations shown by the products of reaction at higher temp. (-20° to 20°) arises from the simultaneous independent formation of *d*- and *l*-isomerides. Details are given for the variation of inversion with temp. for the three carbinols, and rotatory dispersion data are recorded. F. L. U.

Preparation of alkoxy- and aryloxy-ethanols and higher homologues. L. PALFRAY, S. SABETAY, and A. HALASZ (Compt. rend., 1939, 208, 289—291; cf. A., 1934, 990).—CH₂Ph·CH₂·OH with (CH₂)₂O in acid solution gives β-β'-phenylethoxyethyl alcohol, b.p. 140—142°/15 mm. (acetate, b.p. 159—160°/18 mm.; allophanate, m.p. 150°). CH₂PhCl and Ph·[CH₂]₂·Cl heated with OH·[CH₂]₂·OK and excess of (CH₂·OH)₂ afford β-benzyloxy-, b.p. 136—137°/17 mm. (formate, b.p. 150°/21 mm.; acetate, b.p. 145—146°/15 mm.; Bu ether, b.p. 139—140°/15 mm.; allophanate, m.p. 156°), and β-γ'-phenylpropoxy-ethyl

alcohol, b.p. 154—155°/18 mm. (acetate, b.p. 170°/18 mm.; allophanate, m.p. 131·5°), respectively; with $\text{OH} \cdot [\text{CH}_2]_3 \cdot \text{OK}$ γ -benzyloxy-, b.p. 155—157°/20 mm. (acetate, b.p. 154—156°/16 mm.; Bu ether, b.p. 160—162°/32 mm.; allophanate, m.p. 119°), and γ - γ' -phenylpropoxy-propanol, b.p. 160°/20 mm. (acetate, b.p. 182—184°/20 mm.; allophanate, m.p. 113°), respectively, result. Similarly, CH_2PhCl and $\text{Ph} \cdot [\text{CH}_2]_3 \cdot \text{Cl}$ with $\text{OH} \cdot \text{CHMc} \cdot [\text{CH}_2]_2 \cdot \text{OK}$ afford γ -hydroxy- α -benzyloxy-, b.p. 151—152°/18 mm. (acetate, b.p. 170°/25 mm.; allophanate, m.p. 102°), and α - γ' -phenylpropoxy-butane, b.p. 175°/19 mm. (acetate, b.p. 184—185°/18 mm.; allophanate, m.p. 165°). Dodecyl iodide with $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{OK}$ at 300° (autoclave) affords β -dodecyloxyethyl alcohol, m.p. 51°.

J. L. D.

Action of magnesium bromide etherate on 1:2-epoxy-1:4-dimethylcyclohexane. B. TOHOUBAR (Compt. rend., 1939, 208, 355—357).—1:2-Epoxy-1:4-dimethylcyclohexane with MgBr_2 etherate affords trans-2-bromo-1:4-dimethylcyclohexanol (I), b.p. 109—111°/17 mm. (dinitrobenzoate, m.p. 134—135°), and trans-2-bromo-2:5-dimethylcyclohexanol (II) (not isolated). Dehalogenation (MgBr_2) of (I) affords only 3-methylcyclopentyl Me ketone (III) (semipinacolic change), whereas a mixture of (I) and (II) gives (III); 2:5-dimethylcyclohexanone (migration of H), and 1:3-dimethylcyclopentylformaldehyde (semihydrobenzoin change) (corresponding acid amide, m.p. 88°). 2-Methylcyclohexanone (A., 1939, II, 61) is thus formed by migration of H during dehalogenation of 2-bromo-2-methylcyclohexanol. J. L. D.

Oxidation of methine and methylene groups [in cyclic hydrocarbons] by ozone. J. R. DURLAND and H. ADKINS (J. Amer. Chem. Soc., 1939, 61, 429—433).— O_3 in CCl_4 at 0° attacks $\geq \text{CH}$ or $> \text{CH}_2$ in saturated cyclic compounds to give $\geq \text{C} \cdot \text{OH}$ and $> \text{CO}$, respectively. cycloHexane is most resistant, but gives HCO_2H , adipic acid, and cyclohexanone on prolonged treatment. cis-Decahydronaphthalene (30 g.) gives 1-keto- (small amount) and 9-hydroxy-cis-decahydronaphthalene (I) (7·4 g.), $\Delta^{9:10}$ -octahydronaphthalene (II) (2·2 g.), and mixed acids (10 g.); under similar conditions, trans-decahydronaphthalene (34 g.) gives 28% of 9-hydroxy- and 1-keto-trans-decahydronaphthalene [or 21% of (II)], and ~10 g. of acids, including trans-cyclohexane-1:2-diacetic acid. (I) gives HCO_2H and other acids, (II), and a trace of 9:10-dihydroxydecahydronaphthalene, m.p. 86—89°. Mixed dodecahydronaphthalenes give (1-, 4-, or 10-)keto- $\Delta^{11:12}$ -dodecahydronaphthalene (III), b.p. 150—155°/8 mm. (2:4-dinitrophenylhydrazones, forms, m.p. 82—84° and 112—115°), and $\alpha\beta$ -di-2-ketocyclohexylethane (derived from the $\Delta^{12:13}$ -hydrocarbon). Tetradecahydronaphthalene (IV) gives (III), a dodecahydronaphthalene (V), b.p. 129°/9 mm., and mixed acids, or, in another experiment (III), three tetradecahydronaphthalen-11-ol or -12-ols, A, b.p. 130—132°/8 mm., B, b.p. 147—150°/7 mm., and C, b.p. 114—116°/0·4 mm., (?) 1-ketotetradecahydronaphthalen-11-ol (VI), b.p. 145—148°/0·2 mm., and mixed acids. Hydrogenation (Raney Ni) of A or B in methylcyclohexane at 200—250° gives (IV). Dehydration of A gives (V), and that of C gives a similar compound. A,

being most reactive, is probably a trans-isomeride. A, B, and C do not give benzoates and are dehydrated by PhNCO . Hydrogenation of (VI) at 125° gives (?) tetradecahydronaphthalen-1:11-diol, b.p. 190—198°/8 mm.

R. S. C.

Free radicals and radical stability. V. Thermal stability of chloroformates and carbonates. S. T. BOWDEN. VI. Reactions of triphenylmethoxides. S. T. BOWDEN and T. JOHN (J.C.S., 1939, 310—314, 314—317).—V. Attempts to prepare $(\text{CPh}_3)_2\text{CO}_3$ from $\text{CPh}_3 \cdot \text{OK}$ and COCl_2 in PhMe at 0° give an almost quant. yield of CPh_3Cl owing to the thermal instability of the intermediate $\text{ClCO}_2\text{CPh}_3$. $\text{CPh}_3 \cdot \text{OH}$ and COCl_2 in C_6H_6 give CPh_3Cl (76% yield in presence of CaCl_2) (mechanism discussed). $\text{CHPh}_2 \cdot \text{OH}$ and K in boiling xylene in N_2 give the K derivative, which with COCl_2 in PhMe at 0° or at room temp. affords benzhydryl carbonate, m.p. 123°, decomp. in N_2 at 260°, with fairly rapid pyrolysis at 270°. $\text{ClCO}_2\text{CHPh}_2$ could not be isolated, although it is probably formed. $\text{CH}_2\text{Ph} \cdot \text{OK}$ and COCl_2 -PhMe give benzyl carbonate, m.p. 29°, stable at 350° (in N_2). The greater is the radical stability of the ester group in chloroformates or carbonates, the lower will be the thermal stability of the compound.

VI. Compounds containing the radical $\text{CPh}_3 \cdot \text{O} \cdot$ are compared with those containing $\text{CPh}_3 \cdot$. $\text{CPh}_3 \cdot \text{OH}$ and Li in pure N_2 (slow reaction at 280°) or better in xylene (C_6H_6 for 120 hr. is ineffective) give Li triphenylmethoxide, decomp. $> 360^\circ$, hydrolysed by moist air to the carbinol and LiOH. An apparatus is described for the prep. on micro-scale of Rb triphenylmethoxide, m.p. 235° (decomp.). Ca does not react with $\text{CPh}_3 \cdot \text{OH}$ in boiling xylene (cf. Kraus *et al.*, A., 1924, i, 276), but $\text{CPh}_3 \cdot \text{ONa}$ is prepared in xylene or Ph₂ in N_2 (cf. Blicke, A., 1923, i, 1007). $\text{CPh}_3 \cdot \text{OK}$ and CH_2PhBr or Me_2SO_4 in C_6H_6 give $\text{CPh}_3 \cdot \text{O} \cdot \text{CH}_2\text{Ph}$ or $\text{CPh}_3 \cdot \text{OME}$, respectively; Hg in N_2 has no effect (cf. CPh_3K). $\text{CPh}_3 \cdot \text{OH}$, or better, COPh_2 , and MgPhBr , afford $\text{CPh}_3 \cdot \text{O} \cdot \text{MgBr}$ (I), which does not give ethers with CH_2PhBr or MeI , but with $\text{AcCl} \cdot \text{C}_6\text{H}_6$ (through $\text{CPh}_3 \cdot \text{OAc}$) or COCl_2 -PhMe (through the unstable chloroformate), it affords CPh_3Cl (37 and 14% conversions, respectively). (I) and CPh_3Br or CuCl_2 at room temp. give (after hydrolysis) only $\text{CPh}_3 \cdot \text{OH}$. PhOH and MgPhBr give $\text{MgBr} \cdot \text{OPh}$, which with COCl_2 -PhMe at 0° affords Ph_2CO_3 (66% yield); this reaction is a possible method for synthesising carbonates when the usual one is not feasible.

A. T. P.

Constitution of sterols and steroids. A. WINDAUS (Chim. et Ind., 1938, 40, 835—849).—A review.

Colour reactions of sterols. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1939, 22, 47—59; cf. A., 1937, II, 367; 1938, II, 429).—A description is given of the colour reactions of cholic, deoxycholic, glyeochoic, and taurochoic acid, of cholesterol, ergosterol, sitosterol, stigmasterol, œstrone, equilin, equilenin, and œstradiol with furfuraldehyde (I) and conc. H_2SO_4 . With ascorbic acid, which slowly yields (I) under these conditions, the appearance of the colours is greatly retarded.

H. W.

Sterol group. XXXIX. Structures of ergosterol, lumisterol, pyrocalciferol, and isopyrocalciferol. T. KENNEDY and F. S. SPRING (J.C.S., 1939, 250—253; cf. A., 1938, II, 321).—Pyrocalciferol acetate, m.p. 81—82°, $[\alpha]_D^{20} +407^\circ$ in CHCl_3 , and eosin in EtOH in absence of air, irradiated with sunlight (2 weeks), afford pyrocalciferol "pinacol" diacetate, m.p. 196°, $[\alpha]_D^{20} -80^\circ$ in CHCl_3 , which at 180—190° at 0.1 mm., then 0.0001 mm., gives neo-ergosterol acetate, m.p. 121—122°, identical with that prepared similarly from "ergopinacol" diacetate. isoPyrocalciferol acetate is unaffected by similar long irradiation. Lumisterol is also similarly stable (cf. Dimroth, A., 1936, 840). Since ergosterol, dehydroergosterol (Windaus *et al.*, A., 1928, 425, 1372), and dehydrolumisterol acetate (Dimroth, *loc. cit.*) yield bimol. "pinacol" derivatives, orientation around C_{10} is the determining factor in "pinacol" formation. A positive "pinacol" reaction in the ergosterol series indicates a *trans*-orientation of $\text{C}_{10}\text{-Me}$ and $\text{C}_{9}\text{-H}$; with lumisterol, there is *cis*-orientation. Structural formulæ are given.

A. T. P.

Sex hormones and related substances. XII. Comparison of cinchol with sitosterol and stigmasterol. W. DIRSCHERL (Z. physiol. Chem., 1939, 257, 239—245; cf. A., 1938, II, 276; Ruzicka *et al.*, A., 1937, II, 497).—Cinchol (I) is probably identical with β -sitosterol and with 22:23-dihydrostigmasterol (II). Possibly, however, the terminal C_6H_{13} residue of the side-chain of (I) differs from that of (II).

W. McC.

Dihydrotachysterol.—See B., 1939, 325.

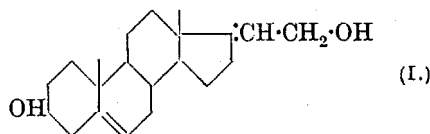
Preparation of iodo-compounds of sterols from sterol alcohols. B. HELFERICH and E. GÜNTHER (Ber., 1939, 72, [B], 338—340).—Cholesterol and MeSO_2Cl in cold anhyd. $\text{C}_5\text{H}_5\text{N}$ give *cholesteryl methanesulphonate* (I), m.p. 121—123°, $[\alpha]_D^{25} -35.7^\circ$ in CHCl_3 , which slowly decomposes at room temp. *Sitosteryl* (II), m.p. 122—123°, $[\alpha]_D^{25} +16.4^\circ$ in CHCl_3 , and *stigmasteryl* (III), m.p. 140—141°, $[\alpha]_D^{25} -47.7^\circ$ in CHCl_3 , *methanesulphonates* are obtained similarly. NaI and (I) in COMe_2 at 60° afford *cholesteryl iodide*, m.p. 104—106°, $[\alpha]_D^{25} -13.4^\circ$ in CHCl_3 , also obtained analogously from *cholesteryl p*-toluenesulphonate. (II) and (III) afford respectively *sitosteryl iodide*, m.p. 100—102°, $[\alpha]_D^{25} +34.0^\circ$ in CHCl_3 , and *stigmasteryl iodide*, m.p. 86—88°, $[\alpha]_D^{25} -26.8^\circ$ in CHCl_3 .

H. W.

Phytochemical hydrogenation of œstrone to α -œstradiol. A. WERTSTEIN (Helv. Chim. Acta, 1939, 22, 250—252).—Gradual addition of œstrone in dioxan to a briskly fermenting mixture of glucose and yeast gives α -œstradiol, m.p. 177—179.5°, $[\alpha]_D^{25} +83^\circ \pm 2^\circ$ in abs. EtOH, in ~70% yield. H. W.

Steroid alcohols with semicyclic double linking. K. MIESCHER and C. SCHOLZ (Helv. Chim. Acta, 1939, 22, 120—125).— Δ^5 -17-Vinylandrosterone-3:17-diol is converted by Ac_2O at 100° followed by addition of $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{AcOH}$ and heating of the mixture at 60° into $\Delta^{5:6-17:20}$ -pregnadiene-3:21-diol (I), m.p. 198—199° [Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at room

temp. give the diacetate (II), m.p. 136.5—137°, and $\Delta^{5:16-20}$ -pregnatrien-3:1-ol, m.p. 125.5—126° (acetate,



m.p. 86.5—87°), after hydrolysis with aq. $\text{MeOH}\cdot\text{K}_2\text{CO}_3$. The constitution of (I) is established by bromination of (II), fission of the semicyclic double linking with O_3 in AcOH , debromination, reacetylation, and conversion of the product into the semicarbazone of 3:17-dehydroandrosterone acetate (in very small amount). 17-Vinyltestosterone is converted similarly by Ac_2O and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ into $\Delta^{4:5-17:20}$ -pregnadien-21-ol-3-one, m.p. 138—139° (acetate, m.p. 107°).

H. W.

Crystalline peroxide of $\Delta^{5:8}$ -androstadiene-3:17-diol [diacetate]. A. BUTENANDT and J. PALAND (Ber., 1939, 72, [B], 424—425).—Irradiation of $\Delta^{5:7}$ -androstadiene-3:17-diol diacetate (A., 1938, II, 322) in 96% EtOH containing eosin gives the peroxide, $\text{C}_{27}\text{H}_{42}\text{O}_6$, m.p. 221—221.5°, $[\alpha]_D^{25} -4.8^\circ$ in CHCl_3 . Addition of O to the conjugated system of the diol causes disappearance of the selective absorption in the ultra-violet.

H. W.

Steroids and sex hormones. XLIX. 17-Acetylenyl- and 17-vinyl-androstane or -androstene derivatives and their oxidation products. L. RUZICKA and K. HOFMANN (Helv. Chim. Acta, 1939, 22, 150—155).—17-Acetylenyl-3-*trans*:17-dihydroxyandrostane diacetate, suspended in EtOH, is hydrogenated ($\text{Pd}\cdot\text{CaCO}_3$) to 17-vinyl-3-*trans*:17-dihydroxyandrostane diacetate, m.p. 156—158°, $[\alpha]_D +20.4^\circ$ in dioxan, ozonised in well-cooled EtOAc and then converted ($\text{H}_2\cdot\text{Pd}\cdot\text{CaCO}_3$) into 17-aldehydo-3-*trans*:17-dihydroxyandrostane diacetate, m.p. 152—156° (semicarbazone). Prolonged treatment of Δ^5 -17-vinyl-3-*trans*:17-dihydroxyandrostene (I) with Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 100° yields the diacetate, m.p. 120—121°, $[\alpha]_D -37.4^\circ$ in dioxan [also obtained by partial reduction ($\text{H}_2\cdot\text{Pd}\cdot\text{CaCO}_3$) of Δ^5 -17-acetylenyl-3-*trans*:17-dihydroxyandrostene diacetate], hydrolysed to (I). $\text{Me } \Delta^5$ -3-*trans*:17-dihydroxyœtiocholenate and $\text{Me } \Delta^5$ -17-hydroxy-3-*trans*-acetoxyœtiocholenate have $[\alpha]_D -62^\circ \pm 2^\circ$ and $-62^\circ \pm 6^\circ$ in dioxan, respectively. All m.p. are corr.

H. W.

Preparation of the principles of the adrenal cortex. A. SERINI, W. LOGEMANN, and W. HILDEBRAND (Ber., 1939, 72, [B], 391—396; cf. A., 1938, II, 322; 1939, II, 112).—Deoxycorticosterone acetate, m.p. 155.5—156.5°, $[\alpha]_D^{25} +177^\circ$ in abs. EtOH, sublimates when Δ^4 -pregnene-17:20:21-triol-3-one 20:21-diacetate is heated with Zn dust at 150—200°/10⁻⁴ mm. 17-Vinylisandrosterone-3:17-diol (I) is converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at room temp. into its 3-monoacetate, m.p. 152—154°, $[\alpha]_D^{25} -5.4^\circ$ in dioxan. (I) is transformed by the successive action of Ac_2O at 100°, $\text{CCl}_3\cdot\text{CO}_2\text{H}$ in AcOH at 40—42°, and $\text{N}\cdot\text{KOH}\cdot\text{MeOH}$ into Δ^{17} -allopregnene-3:21-diol, m.p. 202—204°, $[\alpha]_D^{25} +27.2^\circ$ in dioxan. The diacetate, m.p. 156°, $[\alpha]_D^{25} +23.7^\circ$ in dioxan, is transformed by OsO_4 in Et_2O , followed by hydrolysis (aq. EtOH—

Na_2SO_3), into β -allopregnane-3:17:20:21-tetraol, m.p. 200°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH (3:20:21-triacetate, m.p. 176—177°, $[\alpha]_D^{20} + 53^\circ$ in COMe_2), identical with Reichstein's substance K. The 3:17:20:21-tetrahydroxyallopregnane, m.p. 230—232°, obtained from 17-vinylisoandrostanediol (*loc. cit.*) is shown to be a mixture which can be separated by chromatographic analysis (Brockmann's Al_2O_3) of its acetate into two triacetates, m.p. 146—148°, $[\alpha]_D^{20} \pm 0^\circ$ in COMe_2 , and m.p. 119—120°, $[\alpha]_D^{20} - 32^\circ$ in COMe_2 , which are hydrolysed to the isomeric α -allopregnane-3:17:20:21-tetraols, m.p. 210—211°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH, and m.p. 236—238°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH, respectively. H. W.

Phosphatides. XIV. Inositolmonophosphoric acid from the phosphatide of soya bean. E. KLENK and R. SAKAI (*Z. physiol. Chem.*, 1939, 258, 33—38; cf. A., 1937, III, 56; Cason and Anderson, A., 1939, II, 48).—The isolation from the kephalin fraction of the phosphatide of the Ba salt, $\text{C}_6\text{H}_{11}\text{O}_9\text{P} \cdot \text{Ba} \cdot 2\text{H}_2\text{O}$, is described. The free acid (I), probably $\text{C}_6\text{H}_{13}\text{O}_9\text{P} \cdot 3\text{H}_2\text{O}$ [*brucine salt*, $\text{C}_6\text{H}_{13}\text{O}_9\text{P}(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2$, m.p. 236°], is very hygroscopic. (I) is accompanied by an acid (II), $[\alpha]_D^{20} + 31.9^\circ$ in H_2O , containing ~9% of P, which is probably very closely related to (I). The Ba salt of (II) when freed from PO_4 by boiling with 10% H_2SO_4 yields a substance, m.p. >280°. W. McC.

Preparation of γ -hydroxy- α -p-anisylbutyric acid. M. LAPINÉ (*Bull. Soc. chim.*, 1939, [v], 6, 390—392; cf. Carré *et al.*, A., 1933, 392).— p -OMe- $\text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$ (I) in Et_2O with aq. KI gives the corresponding iodide, converted by NaCN in aq. EtOH at 6—8° into the nitrile, b.p. 157°/21 mm., the Na derivative (prep. by NaNH_2) of which with $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$ in Et_2O gives γ -hydroxy- α -p-anisylbutyronitrile, b.p. 118—120°/4 mm. Hydrolysis [$\text{Ba}(\text{OH})_2$] affords the butyric acid, m.p. 90° (dehydrates readily to form the lactone). (I) and NaCN in aq. EtOH give p -OMe- $\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OEt}$ and a resin. A. T. P.

Polycyclic aromatic hydrocarbons. XIX. J. W. COOK, (MRS.) A. M. ROBINSON, and (MISS) E. M. F. ROE (*J. C.S.*, 1939, 266—268; cf. A., 1938, II, 227).—9:10-Dihydroanthracene (I), $(\text{CH}_2 \cdot \text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 give β -9-(9:10-dihydro)anthrolylpropionic acid (II), m.p. 160—161° [*semicarbazone* (III), m.p. 203—204° (decomp.)], oxidised (CrO_3 -AcOH) to anthraquinone. Thus substitution occurs at a saturated C atom, showing great reactivity of CH_2 in (I); direct replacement of H is the most likely mechanism (cf. Nenitzescu *et al.*, A., 1938, II, 494). That (II) was not β -9-anthrolylpropionic acid was shown by spectroscopic comparison of allied compounds, and by reduction (Wolff-Kishner) of (III) to γ -9-(9:10-dihydro)anthranlylbutyric acid, m.p. 132—133°, dehydrogenated by S at 220—230° to γ -9-anthranlylbutyric acid, m.p. 187.5—188.5° (CrO_3 gives anthraquinone). CH_2Ph_2 and $(\text{CH}_2 \cdot \text{CO})_2\text{O}$ give [as for (I)] β -p-benzylbenzoylpropionic acid, m.p. 125—126° (normal nuclear substitution), oxidised (alkaline KMnO_4) to p - $\text{C}_6\text{H}_4\text{Bz} \cdot \text{CO}_2\text{H}$. A. T. P.

Fission of phenylethylthiolacetic acids. B. HOLMBERG (*Arkiv Kemi, Min., Geol.*, 1938, 12, A,

No. 28, 15 pp.).— $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$ and $\text{CHPhMe} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (I) in aq. Na_2CO_3 at 100° (bath) yield $\text{CHPhMe} \cdot \text{OH}$ (II) and $\text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$; similarly, $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ (III) gives

$\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{S}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O}$, which when heated with NaOH yields CH_2CHPh and $\text{S}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$. When heated with HgCl_2 , (I) gives (II) and chloromercurithiolacetic acid, $\text{ClHgS} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m.p. 202—203° (decomp.), whilst with HgSO_4 -dil. H_2SO_4 , $\text{Hg}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ is formed. With HgSO_4 -dil. H_2SO_4 , (III) yields the compound, $(\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{S})_2\text{Hg} \cdot \text{HgSO}_4$, which when heated with KI gives $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{SH}$ (IV). $\text{CHPhMe} \cdot \text{SH}$ or $(\text{CHPhMe} \cdot \text{S})_2$ with Br in AcOH gives first CHPhMeBr and then $\text{CHPhBr} \cdot \text{CH}_2\text{Br}$ (V), both of which are formed successively from (I) with Br in AcOH. With SO_2Cl_2 , (I) yields CHPhMeCl . Oxidation of (IV) with H_2O_2 affords $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$ and di- β -phenylethyl disulphoxide, m.p. 47.5—48.5°, both of which yield β -phenylethanesulphonyl bromide, m.p. 59—60°, with Br in aq. AcOH. Bromination of the sulphonide of (I) gives a little (V); the sulphone yields α -phenylethyl dibromomethyl sulphone, m.p. 96.5—97.5°. J. D. R.

Styrene, iodine, and dithioacetic acid. B. HOLMBERG (*Arkiv Kemi, Min., Geol.*, 1938, 12, B, No. 48, 3 pp.).—Styrene and $(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ in Et_2O with a little I yield styrenedithiolacetic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m.p. 84—86°. The reaction fails in absence of I, which is apparently a catalyst. J. D. R.

dl-Hexahydrophenylalanine (hydrochloride, m.p. 242—243°); α -acetamido- β -cyclohexylpropionic acid, m.p. 198—199°, $[\alpha]_D^{20} - 4.23^\circ$ in 95% EtOH; α -amino-, m.p. 276° (decomp.), and α -acetamido- γ -cyclohexylbutyric acid, m.p. 195—196°, $[\alpha]_D^{20} + 16.1^\circ$ in 65% EtOH.—See A., 1939, III, 174.

Thermal decomposition of the lead salts of α -hydroxycarboxylic acids. J. KENNER and R. L. WAIN (*Ber.*, 1939, 72, [B], 456—459).—Pb 9-hydroxyfluorene-9-carboxylate darkens at ~125° and gives fluorenone when distilled. $(\text{OH} \cdot \text{CPh}_2 \cdot \text{CO}_2)_2\text{Pb}$ affords $\text{CHPh}_2 \cdot \text{CO}_2\text{H}$, $\text{C}_2\text{H}_5\text{Ph}$, and COPh_2 . Pb cyclohexan-1-ol-1-carboxylate at 310° yields H_2O , cyclohexene, and an oil transformed by HCO_2H into Δ^1 -tetrahydrobenzoic acid (39%), m.p. 33—35° (chloride, b.p. 203—204°; amide, new m.p. 129—130.5°; anilide, m.p. 110—111°). Pb cyclopentan-1-ol-1-carboxylate gives Δ^1 -cyclopentene-1-carboxylic acid (43%), m.p. 119—120° (chloride, b.p. 179—180°/758 mm.; amide, m.p. 206°; anilide, m.p. 125—125.5°). Pb 4-methylcyclohexan-1-ol-1-carboxylate affords 4-methyl- Δ^1 -cyclohexene-1-carboxylic acid (yield ~36%) but no ketone. cycloHeptene (32%) (nitroschloride, m.p. 118°) is obtained from Pb cycloheptan-1-ol-1-carboxylate. H. W.

Adduct, m.p. 110°, of dihydro-*o*-tolualdehyde and maleic anhydride. Dihydro-*o*-toluamide, m.p. 88°. cis- Δ^5 -Tetrahydro-*o*-toluamide, m.p. 104°. Δ^6 -Tetrahydro-*o*-toluamide, m.p. 142°.—See A., 1939, III, 175.

Esters of 3:5-dihydroxybenzoic acid. C. M. SUTER and A. W. WESTON (J. Amer. Chem. Soc., 1939, 61, 531).—Et, m.p. (anhyd.) 128.5°, (+H₂O) ~80° (lit. <100°), Bu^a, b.p. 209—210°/2 mm., m.p. (anhyd.) 62.5—63.5°, (+0.5H₂O) 39—40°, and n-heptyl 3:5-dihydroxybenzoate, b.p. 235—237°/2 mm., m.p. 74—75°, have PhOH coeff. (*S. aureus*) <10, <10, and 38, respectively. The Me, m.p. 163—165°, Pr^a, b.p. 215—217°/3 mm., m.p. (+H₂O) 67—68°, n-amyl, b.p. 225—227°/4 mm., and n-hexyl, b.p. 220—221°/2 mm., m.p. 65—66.5°, esters are also prepared.

R. S. C.

p-Nitrobenzyl 3:5-dinitrosalicylate.—See A., 1939, III, 218.

Halogen derivatives of the methyl ethers of orcinol, p-orsellinic acid, and phloroglucinol-carboxylic acid. C. T. CALAM and A. E. OXFORD (J.C.S., 1939, 280—284).—Me p-orsellinate Me₂ ether and excess of Cl₂ in CCl₄ (Al-Hg couple) at room temp. give Me 2:6-dichloro-3:5-dimethoxy-p-toluic acid (I), m.p. 86—88°, hydrolysed by 0.5N-NaOH-EtOH to a substance, m.p. 235—237° (shrinks at 200°) [probably a polymeride of (II)], which cryst. from boiling H₂O (+ trace of HCl) gives 2:6-dichloro-3:5-dimethoxy-p-toluic acid (II), m.p. 121—122°. (II) and aq. KMnO₄-NaOH give 2:6-dichloro-3:5-dimethoxyterephthalic acid, m.p. 235—237°. Crude (II) and 80% H₂SO₄ at 125—130° give 2:6-dichloro-5-methoxy-m-cresol, m.p. 129—130°, methylated (CH₂N₂) to 2:6-dichloro-orcinol Me₂ ether, m.p. 133—134°, which could not be nitrated (oxidations usually resulted), nor condensed with o-C₆H₄(CO)₂O (AlCl₃). (I) and H₂SO₄-H₂O (2:1) at 125° give 2:6-dichloro-3-hydroxy-5-methoxy-p-toluic acid, m.p. 202—203° [Me ester (HCl method), m.p. 97°]. (II) gives an amide, m.p. 167°, converted by P₂O₅ at 180° into 2:6-dichloro-3:5-dimethoxy-p-tolunitrile, m.p. 124°, but attempts to link it with the orcinol nucleus (Hoesch reaction), or with 1:3:5-C₆H₃Me(OMe)₂ (AlCl₃), failed. 2:4:6:1-(OMe)₃C₆H₂CO₂Me and Cl₂ in CCl₄ give Me 3-chloro-2:4:6-trimethoxybenzoate, m.p. 126—128°. 1:2:3:5-C₆H₂MeBr(OMe)₂ and aq. KMnO₄-NaOH afford (small yield) 2-bromo-3:5-dimethoxybenzoic acid, m.p. 208—210° [Me ester (CH₂N₂), m.p. 59.5—60.5°].

A. T. P.

Action of nitric-sulphuric acids on 5-bromo-3:6-dinitro-p-cumene. II. I. J. RINKES (Rec. trav. chim., 1939, 58, 218—226; cf. A., 1939, II, 111).—Me 5-bromo-3:6-dinitro-2:4-, m.p. 173—174°, and Me 4-bromo-2:5-dinitro-3:6-dimethylbenzoate, m.p. 142°, are prepared from 2:4:5:1- and 2:5:4:1-C₆H₂Me₂BrCO₂Me, respectively, with HNO₃ (d 1.5) and 10% oleum at room temp. —60°. The corresponding acids, m.p. 232° (I) and 233° (II), respectively (mixed m.p. 229°), are similarly obtained in poor yield from the C₆H₂Me₂BrCO₂H at 95°. Me 2-bromo-3:6-dinitro-4:5-dimethylbenzoate (III), m.p. 126°, is synthesised according to the scheme: 3:4:1-C₆H₃Me₂NO₂ → 3:4:1-C₆H₃Me₂NH₂ → (via the Ac derivatives) 4:1:2:5-NH₂C₆H₂Me₂Br (IV) → 5-bromo-4-cyano-o-xylene, m.p. 105°, hydrolysed and methylated to Me 2-bromo-4:5-dimethylbenzoate, m.p. 29°, nitrated to (III). The constitution of (IV) is proved by conversion into 1:2:4:5-C₆H₂Me₂Br₂.

The 5-bromo-3:6-dinitrodimethylbenzoic acid (V) previously described (*loc. cit.*) is a mixture of (I) and (II). Presence of (II) is shown by decarboxylation (quinoline-Cu chromite) of (V) to some 3-bromo-2:5-dinitro-p-xylene, m.p. 97° (nitrated to the 2:5:6-trinitro-compound, m.p. 209°, also synthesised by nitrating 1:4:2-C₆H₃Me₂Br), reduced (SnCl₂ in EtOH-HCl) to 3-bromo-2-nitro-5-amino-p-xylene, m.p. 97—98°, which with HNO₂ in EtOH yields 3-bromo-2-nitro-p-xylene, m.p. 64—65°. Reduction (Fe + H₂SO₄) of this yields 3-bromo-2-amino-, m.p. 58°, brominated (Br in AcOH) to 3:5-dibromo-2-amino-p-xylene. The Me ester, m.p. 173°, obtainable from (V) is that of (I).

A. LI.

Syntheses in the phenanthrene series. I. R. GREWE (Ber., 1939, 72, [B], 426—432).—Condensation of CH₂Ph·CNa(CO₂Et)₂ with 2-chlorocyclohexanone gives a mixture of Et₂ 2-ketocyclohexylbenzylmalonate (I), b.p. 180°/0.3 mm., and α-2-hydroxy-Δ¹-cyclohexenyl-β-phenylpropiolactone (II), b.p. 190°/0.3 mm., m.p. 74°, which is separated into its components only with difficulty. Hydrolysis and subsequent decarboxylation of (I) leads to Et α-2-ketocyclohexyl-β-phenylpropionate (III), b.p. 165°/0.3 mm., m.p. 45° (phenylhydrazones, m.p. 175°; semicarbazones, m.p. 174° and 153°). The non-cryst. free acid (IV) is converted by syrupy H₃PO₄ at 100° into 5:6:7:8:9:10-hexahydrophenanthrene-9-carboxylic acid, m.p. 161°, decarboxylated and dehydrogenated by Pd sponge at 260° to phenanthrene. (IV) is converted by dil. H₃PO₄ into (II). Treatment of (III) with Zn and CH₂Br·CO₂Et gives (II); (IV), however, with an excess of the reagents leads to α-2-hydroxy-2-carbethoxymethylcyclohexyl-β-phenylpropiolactone, b.p. 199—203°/0.3 mm., m.p. 75°. Attempts to open the lactone ring by EtOH were unsuccessful. The corresponding OH-acid could not be obtained by means of alkali, which invariably gives a mixture of the stereoisomeric, unsaturated α-2-carboxymethylene-cyclohexyl-β-phenylpropionic acids, m.p. 179—184° (V) (Me₂ ester, m.p. 68°) and m.p. 215—217° (VI) (Me₂ ester, m.p. 79°). (V) is transformed by syrupy H₃PO₄ into a lactic acid, C₁₇H₂₀O₄, m.p. 146°, whereas under allied conditions (VI) gives an unidentified monocarboxylic acid, C₁₇H₁₈O₃, m.p. 216°. Dry distillation of the Ba salt of (V) or (VI) gives 2-benzyl-3:4-tetramethylene-Δ⁴-cyclopentenone, b.p. 159°/3 mm. (semicarbazone, m.p. 196°; phenylhydrazones, m.p. 128°; oxime, m.p. 115°). Hydrogenation (Pt in AcOH) of (II) gives β-cyclohexyl-α-2-hydroxy-Δ¹-cyclohexenylpropiolactone, b.p. 162°/0.35 mm., converted (MeOH-KOH) into the non-cryst. CO-acid (Et ester semicarbazone, m.p. 155°). CH₂Ph·CH(OMe)₂ is transformed by the successive action of AcCl containing SOCl₂ and Et potassiocyclohexanone-2-carboxylate into β-methoxy-β-2-keto-1-carbethoxycyclohexyl-α-phenylethane, b.p. 170°/0.4 mm.

H. W.

Synthesis of 6-chloro-10-methyl-1:2-benzanthracene and related compounds. M. S. NEWMAN and M. ORCHIN (J. Amer. Chem. Soc., 1939, 61, 245—247).—5-Cyano-10-methyl-1:2-benzanthracene is as carcinogenic as 10-methyl-1:2-benzanthracene, but the 7-CN- and 5- and 7-Cl-derivatives are less active, and the 5-NH₂CO-, 7-CO₂H, and 7-CO₂Me

derivatives are inactive. 1:2- $C_{10}H_6(CO)_2O$ and m - C_6H_4Cl -MgBr in C_6H_5 -Et₂O give 2-*m*-chlorobenzoyl-1-*(I)*, m.p. 189.6—190.2° (31.4%) and 1-*m*-chlorobenzoyl-2-naphthoic acid, m.p. 253.0—253.6° (10.3%), and some of the lactone, $C_{24}H_{14}O_2Cl_2$, m.p. 157.4—158°. Decarboxylation of the acids gives m - C_6H_4Cl -CO- $C_{10}H_7$ - β and - α , respectively, also obtained from m - C_6H_4Cl -MgBr and $C_{10}H_7$ -CN. Addition of MgMeBr to *(I)* in Et₂O- C_6H_6 gives 81% of the lactone, m.p. 113.8—114.8°, of 2- α -hydroxy- α -*m*-chlorophenylethyl-1-naphthoic acid, reduced by Zn dust in aq. EtOH to 2- α -*m*-chlorophenylethyl-1-naphthoic acid, m.p. 160—160.6°. With H_2SO_4 at 15° this gives an unstable anthrone, reduced by Zn dust in aq. NaOH to 6-chloro-10-methyl-1:2-benzanthracene (*II*), m.p. 157.6—158.2° (picrate, m.p. 146.8—147.2°), converted by $CuCN$ - C_5H_5N into 6-cyano-10-methyl-1:2-benzanthracene, m.p. 204.4—205.2°, and thence (H_2SO_4 -AcOH- H_2O) into 10-methyl-1:2-benzanthracene-6-carboxylic acid, m.p. 328—330° (uncorr.; decomp.) (Me ester, m.p. 146.2—147°). 2:1- CO_2H - $C_{10}H_6$ -CO- C_6H_4Cl -*p* (*III*) with 2% Na-Hg in NaOH- H_2O -EtOH, followed by H_2SO_4 and then Zn-aq. NaOH, yields 6-chloro-1:2-benzanthracene (*IV*), m.p. 160.6—161.8°, oxidised to the quinone (*V*), m.p. 201—202°, which is also obtained by oxidising (*II*) and is reduced ($SnCl_2$, AcOH-conc. HCl followed by Zn-NaOH) to (*IV*). (*V*) could not be obtained by ring-closure from (*III*); with $AlCl_3$ -NaCl at 160—165°, 7-chloro-1:2-benzanthraquinone was formed. M.p. are corr. R. S. C.

Methyl and ethyl esters of the stereoisomeric hexahydroisophthalic acids. A. SKITA and R. RÜSSLER (Ber., 1939, 72, [B], 265—272).—Variations in the pressure between 1 and 3 atm. and of the temp. between 20° and 66° do not affect the ratio of *cis*- to *trans*-ester formed by the hydrogenation (Pt- $BaSO_4$) of m - $C_6H_4(CO_2Me)_2$. With increasing age of the catalyst and consequent decreasing rate of hydrogenation the ratio *cis*:*trans*-ester becomes displaced in favour of the more stable and energy-poorer *trans*-form. Separation of the ester mixture is effected after hydrolysis by the action of 25% aq. NH_3 on the Ca salts of the acids. Conversion of the *cis*- (*I*) into the *trans*- (*II*) -acid by conc. HCl under pressure is inconvenient for considerable amounts but an analogous isomerisation is effected by heating (*I*) for 24 hr. at 170—180° whereby an equilibrium mixture of 30% of (*II*) and 70% of (*I*) results. The Me_2 *cis*- (*III*), b.p. 148°/21 mm., and Me_2 *trans*- (*IV*), b.p. 139°/20 mm., Et₂ *cis*- (*V*), b.p. 151°/15 mm., and Et₂ *trans*- (*VI*), b.p. 141.5°/15 mm., -esters differ pairwise considerably in b.p., contrary to von Auwers (A., 1924, i, 513). The very slight differences of *d* and *n* in the cases of (*III*) and (*IV*) and of *d* in those of (*V*) and (*VI*) do not follow the rule of von Auwers, which is followed by *n* of (*V*) and (*VI*). The differences, however, are so small as to be valueless for the determination of configuration. The heats of formation of (*III*) and (*V*) somewhat exceed those of (*IV*) and (*VI*), respectively, but the differences are not very great. The dipole moment of the *cis*- exceeds that of the corresponding *trans*-forms. H. W.

Action of some endosuccinic acids derived from polycyclic hydrocarbons on the red blood

corpuscles of the mouse. F. L. WARREN (Biochem. J., 1939, 33, 165—169).—See A., 1939, III, 350. Maleic anhydride additive compounds (endosuccinic acids) of the following are described: 1:2:3:4-dibenzanthracene, m.p. 250—251°; cholanthrene, m.p. 219—220°; 5:6-cyclopenteno-, m.p. 245—246°, 3-, m.p. 257—258°, 5-, m.p. 252—253°, and 10-methyl-, m.p. 262—264°, 1:2-benzanthracene (all these are *cis*-compounds); also *trans*-1:2:5:6-dibenzanthracene-9:10-endo- $\alpha\beta$ -succinic acid, m.p. 255—257°, and its Me_2 ester, m.p. 179—180°. A. L.

Prehnitic (benzene-1:2:3:4-tetracarboxylic) acid. L. I. SMITH and E. J. CARLSON (J. Amer. Chem. Soc., 1939, 61, 288—291).—No reaction occurs between $(\cdot CH\cdot CH\cdot CO_2R)_2$ ($R = H, Me, \text{ or } Et$) and $(\cdot C\cdot CO_2R)_2$ ($R = H, Me, \text{ or } Et$), $(\cdot CH\cdot CH\cdot CO_2Me)_2$ and $(\cdot CH\cdot CO)_2O$ or benzoquinone, $(\cdot CH\cdot CH\cdot CO_2Et)_2$ and dibromofumaric acid. 1:4- $C_{10}H_6(CO_2H)_2$ and $KMnO_4$ -KOH give 33—40% of 1:2:3:4- $C_6H_2(CO_2H)_4$ [Me_4 ester, m.p. 131—133° (lit. 135°)], which is obtained only in traces by HNO_3 ; CrO_3 -AcOH gives 6% of a yellow substance, m.p. >280°. R. S. C.

Photochemistry of bile acids. III. Ultra-violet irradiation of apocholic, dihydroxycholenic, and isodihydroxycholenic acid. T. S. SHIN (Z. physiol. Chem., 1939, 257, 232—238).—apocholic acid (*I*) in $CHCl_3$ in presence or absence of eosin (*II*) is converted by the light and, when (*II*) or haemin is present (solvent EtOH), slowly by sunlight into dihydroxycholenic acid (*III*). The Me ester of (*III*) in $CHCl_3$ is converted by ultra-violet light into (*I*). Me isodihydroxycholenate (from cholic acid and $ZnCl_2$ in boiling AcOH for 90 min. followed by CH_2N_2) in $CHCl_3$ is not converted by HCl or by light into (*I*) or (*III*). W. McC.

Configuration of the adrenal hormones at C_{17} . K. MIESCHER and A. WETTSTEIN (Helv. Chim. Acta, 1939, 22, 112—117).—Hydrogenation (PtO₂ in EtOH-AcOH) of $Me \Delta^8 3t:17\alpha$ -dihydroxy- Δ^8 -cholesterol (*A*), 1938, II, 492) gives the very hygroscopic $Me 3t:17\alpha$ -dihydroxy- Δ^8 -cholesterol (*II*), m.p. 213—214°, $[\alpha]_D^{20} -1.3 \pm 0.3^\circ$ in MeOH (3t-Ac derivative, m.p. 217—217.5°), which does not give a ppt. with digitonin (*III*) in 60% MeOH. It is hydrolysed (KOH-MeOH) to 3t:17 α -dihydroxy- Δ^8 -cholesterol (*IV*) m.p. 260—262° (decomp.) [Ac_2 derivative, m.p. 227.5—228° (decomp.)]. (*II*) and (*IV*) are not identical with the analogous compounds derived from substance *P* (Reichstein and Gätzi, *ibid.*, 498) and the sole possible reason for the difference is the configurative reversal at C_{17} . In the case of such epimeric compounds the behaviour towards (*III*) is helpful but not decisive. (*I*) and its 3t-Ac derivative have $[\alpha]_D^{20} -50.3 \pm 1^\circ$ and $[\alpha]_D^{15} -54 \pm 4^\circ$ in dioxan, respectively. All m.p. are corr. H. W.

Isolation of a lactone-like compound from the by-products of the oxidation of cholesterol. K. MIESCHER and W. H. FISCHER (Helv. Chim. Acta, 1939, 22, 155—158).—Hydrolysis of the semicarbazones of the subsidiary ketones obtained during the prep. of dehydroandrosterone from cholesterol and removal of norcholestenolone leaves a product from which CH_2Cl_2 removes a *OH*-lactone (*I*), probably

$C_{23}H_{34}O_3$, m.p. 252—254°, probably derived from 3*t*-dihydroxynorcholenic acid or 3*t*-dihydroxycholeonic acid. Although (I) is found in the ketonic portion, it cannot be caused to react with $NH_2 \cdot CO \cdot NH \cdot NH_2$. The presence of OH is established by the formation of an *acetate*, m.p. 218—219°, and a *benzoate*, m.p. 243—244°. Bromination of (I) followed by oxidation (CrO_3 in AcOH) and debromination gives a *ketone*, $C_{23}H_{32}O_3$, m.p. 206—207° (*semicarbazone*, decomp. 270—290° after becoming brown at >250°), which does not give a colour with $C(NO_2)_4$. H. W.

Saponins. IV. Saponin of the fruits of one of the Chinese gleditsias. K. FUJII and T. MATSUKAWA (J. Pharm. Soc. Japan, 1935, 55, 1322—1330).—The fruits of Chinese gleditsia yielded a saponin gledinin, hydrolysed to *gledigenin*, $C_{29}H_{46}(OH) \cdot CO_2H$ (I), m.p. 310° (decomp.) [*Et ester*, m.p. 203° (*acetate*, m.p. 184°); *acetate*, m.p. 264°; *isoacetate*, m.p. 190°; *benzoate*, m.p. 217°; *bromolactone*, m.p. 235° (decomp.); *monoacetylbromolactone*, m.p. 200° (decomp.); *acetyl-lactone*, m.p. 279° (decomp.)]. (I) has one double linking $\alpha\beta$ or $\beta\gamma$ to the CO_2H . Previous work on gleditsia-saponin is reviewed. M.p. are corr. CH. ABS. (c)

"Steric hindrance" in the reactions of aromatic aldehydes. G. LOCK (Ber., 1939, 72, [B], 300—304).— $C_6Cl_5 \cdot CHO$, m.p. 202.5° (corr.), gives a *H sulphite* compound when its solution in C_6H_6 is shaken with aq. $NaHSO_3$; the compound is not obtained from the solid aldehyde probably owing to its sparing solubility in aq. $NaHSO_3$. Under normal conditions $C_6Cl_5 \cdot CHO$ is transformed into the *anil*, m.p. 187.5° (corr.), *oxime*, m.p. 201° (corr.), and *phenylhydrazone*, m.p. 152.5° (corr.). Boiling 1.5% $HCl-EtOH$ converts $C_6Cl_5 \cdot CHO$ into *pentachlorobenzaldehyde Et₂ acetal*, m.p. 45° (yield 60% after 96 hr.); similarly 2:6:1- $C_6H_3Cl_2 \cdot CHO$ affords 2:6-*dichlorobenzaldehyde Et₂ acetal*, b.p. 142—144°/10 mm., m.p. ~ -1° (yield 13.6% after 24 hr. and 43% after 96 hr.). $CHPh(OEt)_2$ is produced in 43% yield after 24 hr. $C_6Cl_5 \cdot CHO$ is oxidised by alkaline $KMnO_4$ to *pentachlorobenzoic acid*, m.p. 208° (corr.), in 90% yield. With Ac_2O and $NaOAc$ at 170—180° $C_6Cl_5 \cdot CHO$ affords *pentachlorocinnamic acid*, m.p. 233° (corr.), in 30% yield after 60 hr. With $MgMeI$ and $MgPhBr$ respectively $C_6Cl_5 \cdot CHO$ yields *pentachlorophenylmethylcarbinol*, m.p. 126°, and 2:3:4:5:6-*pentachlorobenzhydrol*, m.p. 117° (oxidised by CrO_3 to 2:3:4:5:6-*pentachlorobenzophenone*, m.p. 154°). Hindrance of a reaction of $\cdot CHO$ in $C_6Cl_5 \cdot CHO$ is never observed. H. W.

γ -Substitution in the resorcinol nucleus. III. 2:6-Dihydroxy-3-ethylbenzaldehyde. H. A. SHAH and R. C. SHAH (J.C.S., 1939, 300—302).—2:4:5:1- $(OH)_2C_6H_2Et \cdot CO_2Me$ and $Zn(CN)_2-AlCl_3-HCl-Et_2O$ at 0° (method: A., 1939, II, 22) give *Me 2:4-dihydroxy-3-aldehydo-5-ethylbenzoate* (I), m.p. 84—86° [2:4-*dinitrophenylhydrazone*, m.p. 253—254° (decomp.); *semicarbazone*, m.p. 279—280° (decomp.)], hydrolysed by 15% $NaOH$ at room temp. (72 hr.) to the *acid*, m.p. 192—195° (decomp.), and thence by H_2O at 95—100° (sealed tube) to 2:6-*dihydroxy-3-ethylbenzaldehyde*, m.p. 117—118°. (I) and $CH_2(CO_2Et)_2$ or $CH_2Ac \cdot CO_2Et$ (+ a little piperidine) give *Me 5-*

hydroxy-3-carbethoxy- m.p. 138°, and 5-*hydroxy-3-acetyl-*, m.p. 138—140°, -8-*ethylcoumarin-6-carboxylate*, respectively, insol. in aq. alkali. (I) (Clemmensen) gives *Me 2:6-dihydroxy-5-ethyl-m-toluate*, m.p. 164—166°, hydrolysed by 20% $NaOH$ (50 hr.) to the *acid*, m.p. 244—246° (decomp.). A. T. P.

Condensation of furan compounds. IX. Eutectics of ketone-phenol systems and oxonium complex formation. V. V. TSCHELINCEV and G. KUSNETZOV (Bull. Soc. chim., 1939, [v], 6, 256—265; cf. A., 1924, i, 929; Bennett *et al.*, A., 1936, 1241).—M.p. curves indicate the existence of 2:1 mol. compounds of furfurylideneacetone with *p*- $C_6H_4(OH)_2$ and of $CHPh \cdot CH \cdot COMe$ with *o*-, *m*-, and *p*- $C_6H_4(OH)_2$. Similarly, 2:1 complexes of difurfurylideneacetone (I) with *m*- $C_6H_4(OH)_2$, 1:1 complexes of (I) with *m*- and *p*- $C_6H_4(OH)_2$, and 1:2 complexes of (I) with *o*- $C_6H_4(OH)_2$ and of $CO(CH \cdot CHPh)_2$ with *o*-, *m*-, and *p*- $C_6H_4(OH)_2$ are indicated. The CO probably undergoes oxonium salt formation. A. T. P.

Derivatives of 2:4-dimethylphenylacetic acid. G. FRANÇAIS (Ann. Chim., 1939, [xi], 11, 212—243).—2:4:1- $C_6H_3Me_2 \cdot CH_2 \cdot CO_2H$ (I) (prep. from pinene described) is transformed by $SOCl_2$ into the chloride, b.p. 132—134°/25 mm.; this is dissolved in PhMe and added to a solution obtained by adding $ZnCl_2$ in Et_2O to an ethereal solution of the requisite Grignard reagent and replacing the Et_2O by PhMe, thus giving a mixture of $C_6H_3Me_2 \cdot CH_2 \cdot COR$ and $C_6H_3Me_2 \cdot CH_2 \cdot CO_2R$ from which the ester is removed by hydrolysis. The following ketones are described: α -2:4-dimethylphenyl-propan- β -one (II), b.p. 121—123°/14 mm. [*semicarbazone*, m.p. 164°; *oxime*, m.p. 79° (block)]; -butan- β -one (III), b.p. 132.5—134°/15 mm. [*semicarbazone*, m.p. 134—135° (block); *oxime* (IV), m.p. 99—100° (block)]; -pentan- β -one, b.p. 143.9—145.4°/14 mm. (*semicarbazone*, m.p. 174°; *oxime*, m.p. 90—91°); -hexan- β -one (V), b.p. 152—153.5°/13 mm. (*semicarbazone*, m.p. 160°; *oxime*, m.p. 60—61°); Ph 2:4-dimethylbenzyl ketone, m.p. 109° (*semicarbazone*, m.p. 126—127°; *oxime*, m.p. 113°); α -phenyl- γ -2:4-dimethylphenylpropan- β -one, m.p. 85—86° (*oxime*, m.p. 122—123°). Passage of (I) and AcOH over ZrO_2 at 460—480° gives (II), 1:2:4- $C_6H_3Me_2$, and α - γ -di-2:4-dimethylphenylpropan- β -one, b.p. 215°/15 mm., m.p. 66—67° (block) [*oxime*, m.p. 90.5—91° (block); *semicarbazone*, m.p. 134°]; (III) is obtained similarly by using $EtCO_2H$. Reduction ($Zn-Hg$ and HCl in $H_2O-EtOH$) of (V) affords 2:4-dimethylhexylbenzene, b.p. 131—133°/13 mm. Hydrogenation (Ni) of (IV) gives β -amino- α -2:4-dimethylphenylbutane, b.p. 126—127°/15 mm. (*hydrochloride*, m.p. 170°; *nitrate*, m.p. 142—143°; *picrate*, m.p. 145—146°). Reduction (Ni-Pt in EtOH) of the requisite ketone affords the following carbinols: α -2:4-dimethylphenyl-propan- β -ol, b.p. 126.5—128.5°/14 mm. (*allophanate*, m.p. 183—184°); -butan- β -ol, b.p. 140.5°/14 mm. (*allophanate*, m.p. 136—137°); -pentan- β -ol, b.p. 147.2—149.2°/18 mm. (*allophanate*, m.p. 146—147°); -hexan- β -ol, b.p. 156—157.5°/13 mm. (*allophanate*, m.p. 100—101°); α -phenyl- β -2:4-dimethylphenylethan- α -ol, b.p. 191—193°/13 mm. (*allophanate*, m.p. 180—181°), converted by successive

treatment with HBr and KOH-EtOH into 2:4-dimethylstilbene, m.p. 40—41°. H. W.

Reaction of chlorosulphonic acid with acetophenone. Synthesis of a cyclic keto-sulphone. A. W. WESTON and C. M. SUTER (J. Amer. Chem. Soc., 1939, 61, 389—391).—Contrary to Riesz *et al.* (A., 1928, 1009), CPhMe and ClSO₃H in CCl₄, first at 0° and then at 110°, give *acetophenone-2:ω-disulphonyl chloride* (I), m.p. 194—195°, the structure of which is proved by conversion of the corresponding Na₂ salt by KOH at 250—300° into *o*-OH·C₆H₄·CO₂H, and by hot H₂O into 2-keto-1:2-dihydrothionaphthen *S*-dioxide and thence (20% NaOH) into *o*-MeSO₂·C₆H₄·CO₂H. CPhMe and 45% oleum give a product, converted by KOH into *o*- and *m*-OH·C₆H₄·CO₂H. CPh·CH₂·SO₃Na and ClSO₃H give (I). R. S. C.

Benzoylmesitylacetylene. R. C. FUSON, G. E. ULLYOT, and J. L. HICKSON (J. Amer. Chem. Soc., 1939, 61, 410—412).—2:4:6-C₆H₂Me₃·C(OMe)·CH·CN and MgPhBr give an amorphous product, converted by boiling AcOH into 2:4:6-C₆H₂Me₃·CO·CH₂·CPh·NH and by boiling 95% EtOH into *benzoylmesitylacetylene* (I), m.p. 72° (semicarbazone, m.p. 171—172°) (cf. A., 1938, II, 326). With O₃, (I) in CCl₄ gives an ozonide, converted by H₂O₂ into BzOH, β-isodurylic acid, and a little 2:4:6-C₆H₂Me₃·CO·CPh. With H₂-Raney Ni in EtOH at 2.67 atm. (I) gives α-benzoyl-β-mesityl-ethane [β-mesitylpropiophenone], m.p. 85—85.5°, also obtained from CPh·[CH₂]₂·Cl, *s*-C₆H₃Me₃, and AlCl₃ in CS₂ or, by way of Et α-benzoyl-β-mesitylpropionate, b.p. 225—230° (partial decomp.)/23 mm., from CHNaBz·CO₂Et and 2:4:6-1-C₆H₂Me₃·CH₂Cl. With MgPhBr, (I) gives α-hydroxy-α-diphenyl-γ-mesityl-Δ^β-propinene, m.p. 97.5—98.5°, which absorbs 3 H₂ (PtO₂). With H₂SO₄ at room temp. (I) gives 2:4:6-C₆H₂Me₃·CO·CH₂·COPh. 2:4:6-C₆H₂Me₃·C(CN) and BzCl in Et₂O, first at -15° and then at 35°, give (I). R. S. C.

Condensation of paraformaldehyde with aromatic ketones. II. Mesityl ketones. R. C. FUSON, W. E. ROSS, and C. H. MCKEEVER (J. Amer. Chem. Soc., 1939, 61, 414—417; cf. A., 1939, II, 68).—2:4:6-1-C₆H₂Me₃·COMe, paraformaldehyde, and K₂CO₃ in MeOH give 75% of β-hydroxypropionylmesitylene (I), b.p. 132—135°/4 mm., and βδ-di-2:4:6-trimethylbenzoyl-Δ^{αγ}-pentadiene (II), m.p. 107°. (I) reduces Benedict's and Tollens' reagents, with PhNCO gives CO(NHPh)₂, and with BzCl gives only BzOH and a resin. With KMnO₄ (I) gives 2:4:6-C₆H₂Me₃·CO·CO₂H; with HCl it gives β-chloropropionylmesitylene, b.p. 137—139°/3 mm., which readily loses HCl. When 2:4:6-C₆H₂Me₃·COEt and paraformaldehyde are condensed by K₂CO₃ in EtOH, dehydration also occurs to give 70% of mesityl isopropenyl ketone, b.p. 90—95°/3 mm., reduced by H₂-Raney Ni in EtOH to 2:4:6-C₆H₂Me₃·COPr^δ (III), b.p. 107—110°/5 mm., identified as (NO₂)₂-derivative. With paraformaldehyde and K₂CO₃ in EtOH (III) gives 40% of β-hydroxy-α-dimethylpropionylmesitylene, b.p. 153°/7 mm. (phenylurethane, m.p. 116—116.5°). 2:4:6-C₆H₂Me₃·COMe, 40% CH₂O, and NaOH in MeOH give 35% of (II) and much resin.

[CH₂]₃(CO₂H)₂ and SOCl₂ give the dichloride, which with mesitylene and AlCl₃ in CS₂ gives α-diketo-α-dimesitylpentane, m.p. 132—133°, converted by paraformaldehyde and K₂CO₃ in hot EtOH into (II). In presence of Raney Ni in EtOH (II) absorbs 2 H₂ to give βδ-di-2:4:6-trimethylbenzoylpentane, b.p. 228—230°/4 mm., and other products. In CCl₄ (II) absorbs only 2 Br, giving only a dibromide, m.p. 108.5—109.5°, from which NaI in COMe₂ regenerates (II). In presence of ZnCl₂ (II) absorbs 2 AcCl, giving a compound, C₂₃H₃₄O₄Cl₂, m.p. 177—178°. HNO₃-H₂SO₄ converts (II) into a substance, C₂₅H₂₄O₂(NO₂)₄, m.p. 258—259°. (2:4:6-C₆H₂Me₃·CO·CH₂·CH₂)₂, paraformaldehyde, and K₂CO₃ in EtOH give βε-di-2:4:6-trimethylbenzoyl-(?)Δ^{βδ}-hexadiene, m.p. 122—123°. R. S. C.

Synthesis of mixed benzoin. III. R. C. FUSON, W. S. EMERSON, and H. H. WEINSTOCK, jun. (J. Amer. Chem. Soc., 1939, 61, 412—413; cf. A., 1936, 1110).—2:4:6-C₆H₂Me₃·CO·CHO, the appropriate hydrocarbon, and AlCl₃ in CS₂ give 2:4:6-C₆H₂Me₃·CO·CHPh·OH (57%), new m.p. 103.5—104.5°, 2:4:6:4'-tetra- (24%), m.p. 95—95.5°, 2:4:6:2':4'-penta- (17%), m.p. 120—120.5°, and 2:4:6:2':4':6'-hexa-methylbenzoin (40%), m.p. 130.5—131° (lit. 59—60°). The time of heating is very important. *m*-Xylene in CS₂ gives also 34% of 2:4:6-trimethylbenzoyldi-*m*-4-xylylmethane, m.p. 146.5—147°, which is the only product if excess of *m*-xylene is used as solvent. 1:3:5-C₆H₃Me₂·OMe and -C₆H₂Me₂·OEt give only 2:4:6-trimethylbenzoyldi-(6-methoxy-2:4-dimethylphenyl)methane, m.p. 155.5—156.5° [with (?) mesityldi-(6-methoxy-2:4-dimethylphenyl)carbinol, m.p. 185.5—186.5°], and 2:4:6-trimethylbenzoyldi-(6-ethoxy-2:4-dimethylphenyl)methane, m.p. 168—169°, respectively. *s*-C₆H₃Et₃, durene, and isodurene either do not react or give tars. 2:4:6:4'-Tetra-, m.p. 102.5—103°, and 2:4:6:2':4'-penta-methylbenzil, m.p. 84.5—85°, are prepared. R. S. C.

Arylglyoxals and steric hindrance. R. C. FUSON, W. S. EMERSON, and H. W. GRAY (J. Amer. Chem. Soc., 1939, 61, 480—482).—With *o*-C₆H₄(NH₂)₂ in AcOH α-naphthyl- (prep. from α-C₁₀H₇·COMe and SeO₂ in hot, moist dioxan), b.p. 142—145°/6 mm. (hydrate, m.p. 89—91°; 2:4-dinitrophenylhydrazone, m.p. 246.5—247.5°), and *m*-4-xylyl-glyoxal (similarly prepared), b.p. 118—123°/13 mm. (2:4-dinitrophenylhydrazone, m.p. 180—181°), give 2-α-naphthyl-, m.p. 116—116.5° (corr.), and 2-*m*-4-xylyl-quinazoline, m.p. 56—57° (corr.), respectively, but 2:4:6-C₆H₂Me₃·CO·CHO (I) and 2:4:6-triethylphenylglyoxal (II) (prep. as above), b.p. 125—130°/10 mm., stable (oxime, m.p. 107—107.5°), give NN'-dimesityl-, m.p. 183—184° (corr.), and NN'-di-2':4':6'-triethylphenylglyoxylidene-*o*-phenylenediamine, m.p. 136—136.5° (corr.), respectively. With HCl-aq. EtOH (I) gives the *Et* hemiacetal (III), m.p. 55—55.5°, which reduces Tollens' reagent, decomposes in hot C₆H₆, with NH₂OH gives the oxime of (I), and with NaOMe-MeOH and a little I gives 2:4:6-C₆H₂Me₃·CH(OH)·CO₂Me. *Et* mesitylglucolate, m.p. 53.5—54°, prepared for comparison from the acid by HCl-EtOH, depresses the m.p. of (III). With Al(OPr^δ)₃-Pr^δOH (I) gives

Pr⁸ mesitylglycollate, b.p. 122—124°/2 mm., m.p. 62.5—63.5°, readily hydrolysed to the acid. Hot NaOEt-EtOH converts (II) into 2:4:6-triethylphenylglycollic acid, m.p. 91—92°. R. S. C.

Kinetic study of Friedel-Crafts benzophenone synthesis.—See A., 1939, I, 205.

Secondary reactions in the condensation of organo-magnesium compounds with phenylhydrazones. P. GRAMMATICAKIS (Compt. rend., 1939, 208, 287—289; cf. A., 1936, 837; 1938, II, 283).—MgPhBr with CHPh:N:NHPh (I) affords NH₂Ph and NH:CPH₂ as the main secondary reaction products. Similarly, the phenylhydrazones of *p*-C₆H₄Me·CHO and *p*-OMe·C₆H₄·CHO afford *p*-C₆H₄Me·CPH:NH (II) and *p*-OMe·C₆H₄·CPH:NH (III) respectively, and NH₂Ph. (II) and (III) are also obtained from (I) and *p*-C₆H₄Me·MgBr and *p*-OMe·C₆H₄·MgBr, respectively. The above phenylhydrazones with MgEtBr similarly afford NH₂Ph and NH:CPH₂Et, *p*-C₆H₄Me·CET:NH, and *p*-OMe·C₆H₄·CET:NH, respectively, also obtained from CHET:N:NHPh and MgArBr. (I) with MgMeI affords NH₂Ph and NH:CPHMe. Small amounts of anils may be formed by reaction of the ketimines with NH₂Ph. J. L. D.

Metallic derivatives of hydrazones and of the oxime-hydrazones of benzil. T. W. J. TAYLOR, (MRS.) N. H. CALLOW, and C. R. W. FRANCIS (J.C.S., 1939, 257—263).—Benzilmonohydrazone (I) and Ni(OAc)₂ in EtOH or COMe₂ give a Ni complex, decomp. ~200—230°, probably (C₁₄H₁₁ON₂)₂Ni (% Ni very variable), not formed in presence of AcOH. It is decomposed by HNO₃, giving either benzil or (COPh·CPh:N)₂. It is almost certainly not a salt and Ni is probably held by two covalencies and two co-ordinate linkings. (I) also forms a Pd complex, but no complex with Cu, Co^{II}, or Co^{III} salts. Benzilmonophenylhydrazone and Ni(OAc)₂ in C₅H₅N give only a dark red colour (not in EtOH) destroyed by H₂O; the -monophenylmethylhydrazone or -semicarbazone does not give a colour in EtOH or C₅H₅N. No complex formation is noted with deoxybenzoin- or benzoin-hydrazone. Benzildihydrazone in EtOH affords a Ni complex (Ni, 19.3%), decomposed by H₂O. No solid Ni complex was isolated from β-camphorquinonehydrazone (II), which gives (in EtOH) a red colour not observed with the α-isomeride. COMeBu^r and SeO₂ at 110—120° give tert.-butylglyoxal hemihydrate, m.p. 85°. Its monohydrazone (III), m.p. 81°, and Ni(OAc)₂ in EtOH (+ aq. NH₃) yield a complex (21.5% Ni; R₂Ni₂), decomposed by H₂O. This suggests that the stereochemical configurations of (I) and (III) are the same as that of (II), i.e., complex formation involves formation of a 6-membered ring, Ni being attached to O by a co-ordinate linking and to N by a covalent linking, replacing H. Benzil and COMe₂·N·NH₂ in EtOH, or (I) and COMe₂ [+ a little Ni(OAc)₂ (essential)] give benzil acetone azine (IV), COPh·CPh:N·N·CMe₂, m.p. 86°, which does not undergo complex formation with Fe, Ni, or Co. (IV), Ni(OAc)₂, and (I) in EtOH, or better, (I)-Ni(OAc)₂-EtOH-COMe₂, afford an azine Ni complex, C₃₁H₂₆O₂N₄Ni, containing the ·N·CMe₂·N· group (alternative structures discussed); no similar Pd

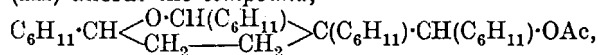
complex is formed. (I) and PhCHO-EtOH yield benzil benzaldehyde azine, COPh·CPh:N·N·CHPh, m.p. 151°, which does not give a Ni complex analogous to the above. Salicylidenehydrazone forms complexes of type R₂Ni and R₂Cu, decomposed by mineral acids,

AcOH, or NH₃. α-Benzil-mono-oxime-hydrazone (V), m.p. 216°, forms metallic complexes (Ni, Co, Cu) in C₅H₅N or dioxan, but the β-isomeride does not (configurations discussed). Aq. FeSO₄ or Co(OAc)₂ and (V) give a Fe^{II} (A), C₂₈H₂₄O₂N₆Fe·2H₂O, and a Co^{II} complex, m.p. 119° (formed more slowly from chloropentamminocobaltic chloride). The above hydrazone complexes are amorphous (except azine complex), whereas metallic derivatives of the oximes crystallise well. A. T. P.

Non-incidence of furan ring-closure in the dehydration of αδ-diketones. H. KLEINFELLER and H. TROMMSDORFF (Ber., 1939, 72, [B], 256—262).—COPh·CO·CHPhBr (I) is transformed by CHNaBz₂ in COMe₂ at 0° into αβε-triketo-δ-benzoyl-αγε-triphenyl-n-pentane, m.p. 138°, which is unchanged when its solution in boiling AcOH or Ac₂O containing ZnCl₂ is treated with HCl, or by warm conc. H₂SO₄; with o-C₆H₄(NH₂)₂ it gives 2-phenyl-3-β-dibenzoyl-α-phenylethylquinoxaline, m.p. 176°, hydrolysed by Ba(OH)₂ in boiling MeOH to 2-phenyl-3-β-benzoyl-α-phenylethylquinoxaline, m.p. 148°. o-C₆H₄(NH₂)₂ and (I) in EtOH afford 2-phenyl-3-α-bromobenzylquinoxaline, m.p. 109—110°. CH₂Ph·CO·CHPhBr and CHNaBz₂ in COMe₂ afford βε-diketo-δ-benzoyl-αγε-triphenyl-n-pentane, m.p. 138°, accompanied by more or less 4-benzoyl-2:3:5-triphenyl-Δ²-cyclopentenone (II), m.p. 192°, which is formed by the action of HCl on the triketone in boiling AcOH; it does not give a hydrazone or phenylhydrazone and is not attacked by Br even when irradiated. The successive action of NaNH₂ and I on CO(CH₂Ph)₂ in abs. Et₂O leads to βε-diketo-αγδζ-tetraphenyl-Δ⁷-hexene, m.p. 196—197°, and 2:4:5-triphenyl-3-benzyl-Δ²-cyclopentenone, m.p. 147—148°. The last substance is also obtained from CO(CH₂Ph)₂, NaOMe, and CH₂Ph·CO·CHPhBr in MeOH. It does not give a phenylhydrazone or a hydrazone and with Br in warm CHCl₃ gives much HBr and resin. CO(CH₂Ph)₂ is converted by NaOEt in boiling EtOH into BzOH, OH·CH(CH₂Ph)₂, and β-keto-δ-benzyl-αγε-triphenyl-Δ⁷-pentene, a colophony-like mass, b.p. 220—240°/0.2 mm. Warm conc. HNO₃ converts (II) into γδ-dinitro-αβε-triketo-δ-benzoyl-αγε-triphenylpentane, complete decomp. 120° after softening at 80—85°. Oxidation of (II) by KMnO₄ in COMe₂ yields BzOH and a product which with EtOH-N₂H₄·H₂O gives (mainly) 6-benzoyl-3:5-diphenyldihydropyridazine hydrazone, decomp. 160—170°. H. W.

Dehydration of acetylenic glycols. H. KLEINFELLER (Ber., 1939, 72, [B], 249—256; cf. A., 1929, 929).—αζ-Diketo-αβζ-tetraphenyl-Δ⁷-hexinene-βε-diol (I) is converted by Br in CHCl₃ into αβζ-tetraphenyl-Δ⁷-hexinene-αζ-trione (II) [monosemicarbazone, m.p. 242° (decomp.)] and benzil. Conc. H₂SO₄ at 80° transforms (I) into ααγ-tribenzoyl-

α -phenyl- Δ^8 -propinene (III), colourless needles or leaflets, m.p. 264° , with smaller amounts of isomeric substances, m.p. 228° (IV) and 178° (V). Under similar conditions (II) is converted by conc. H_2SO_4 into a compound, $\text{C}_{30}\text{H}_{20}\text{O}_3$, m.p. 230° . (II) is oxidised by KMnO_4 in COMe_2 to (III), also obtained from (V) and NH_2OH in boiling EtOH. MgMeBr converts (III) into $\alpha\alpha$ -dibenzoyl- $\alpha\delta$ -diphenyl- Δ^8 -pentinene- δ -ol, m.p. 218° . Catalytic hydrogenation (PtO_2 in AcOH) of (III) affords the compound,



a resin which softens at 30° and could not be induced to crystallise. 3:4-Diphenylfuran-2-carboxylic acid is converted by PCl_5 in C_6H_6 into the corresponding chloride, m.p. $155\text{--}156^\circ$, which with AlCl_3 and C_6H_6 yields 2-benzoyl-3:4-diphenylfuran, m.p. 128° ; Bz can be removed from this product by hydrolysis whereas this reaction is not possible if Bz is attached to $\text{C}_{(3)}$ or $\text{C}_{(4)}$. Addition of 4:4'-dibromobenzil in CHCl_3 to well-cooled ($\text{C}\cdot\text{MgBr}$) $_2$ (VI) in the same solvent yields $\alpha\zeta$ -diketo- $\alpha\beta\zeta$ -tetra-*p*-bromophenyl- Δ^7 -hexinene- $\beta\epsilon$ -diol (VII), m.p. 232° , which is stable towards HCl -EtOH but isomerised and not dehydrated by conc. H_2SO_4 to a substance, $\text{C}_{30}\text{H}_{18}\text{O}_4\text{Br}_4$, m.p. 206° . Boiling aq. NaOH transforms (VII) into $\alpha\delta$ -di-*p*-bromophenyl- Δ^8 -butinene- $\alpha\delta$ -diol, m.p. 181° , and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$. α -Keto- $\alpha\beta$ -di-*p*-bromophenyl- Δ^7 -butinene- β -ol, m.p. 208° , is obtained as by-product in the prep. of (VII). Ac_2 and (VI) in CHCl_3 give β -keto- γ -methyl- Δ^8 -pentinene- γ -ol, b.p. $95^\circ/18$ mm., and β -keto- ζ -acetyl- γ -methylhept- Δ^7 -en- Δ^8 -inen- γ -ol, m.p. 179° . (VI) and $(\text{CH}_3\text{Ac})_2$ afford β -keto- ϵ -methyl- Δ^7 -heptinene- ϵ -ol, b.p. $75^\circ/15$ mm. β -Keto- δ -methyl- $\gamma\gamma$ -diethyl- Δ^6 -hexinene- δ -ol, b.p. $135^\circ/760$ mm., is derived from (VI) and diethylacetylacetone. H. W.

**Constitution of the so-called "phenoldiphen-
ein."** E. H. HUNTRESS and G. E. MOOS (J. Amer. Chem. Soc., 1939, 61, 526-527).—Bachmann's 2:2'-di-*p*-anisoyldiphenyl (A., 1932, 745) is identical with Underwood's "phenoldiphen-*ein* lactone Me_2 ether." All the "diphen-*ein*s" of the latter author (A., 1924, i, 176, 1197; 1930, 1580; 1936, 723) are thus 2:2'-diaroyldiphenyls (cf. Bell *et al.*, A., 1938, II, 495).

R. S. C.

2-Alkylidene- and 2-alkyl-cyclopentanone.—See B., 1939, 244.

Stereochemistry of cyclanes. VII. Stereoisomeric diar[alk]ylcyclanones and spatial structure of their oximes. R. CORNUBERT, M. ANDRÉ, M. DE DEMO, R. JOLY, and A. STRÉBEL. **VIII. 2:6-Dibenzyl- and -dihexahydrobenzyl-cyclohexanones.** R. CORNUBERT, M. ANDRÉ, and M. DE DEMO. **IX. 2:5-Dibenzyl- and -dihexahydrobenzyl-cyclopentanones.** R. CORNUBERT, M. DE DEMO, R. JOLY, and A. STRÉBEL (Bull. Soc. chim., 1939, [v], 6, 103-113, 113-132, 132-143; cf. A., 1939, II, 70).—VII. Parts VIII, IX (below), and X (following abstract) are summarised.

VIII. Reduction (H_2 , Ni, EtOH) of 2:6-dibenzylidenecyclohexanone yields the 2:6-dibenzyl-ketones, m.p. 122° (I) and 55° (II) (Borsche, A., 1912, i, 194; Cornubert *et al.*, A., 1929, 560; 1934, 297), either of which with NaOH , NaOEt , or HCl gives an equilibrium

mixture of the two [$\sim 78\%$ of (I)], and when heated at $>80^\circ$ gives a mixture (composition varies with temp.). (I) and (II) give mixtures of the same two oximes in proportions varying with conditions; both oximes are hydrolysed to mixtures of (I) and (II), the proportions of which show that the oxime of (I) has m.p. 92° (another form, stable at room temp., m.p. 114°), and that of (II), 183° . (I) and (II) yield the same semicarbazone, m.p. $197\text{--}198^\circ$, tetrahydropyrone derivative (using excess of PhCHO), m.p. $177\text{--}178^\circ$, and ($\text{Na} + \text{EtOH}$) sec.-alcohol, m.p. 123° (phenylurethane, m.p. $142\text{--}143^\circ$); catalytic reduction in neutral or acid solution causes hydrogenation of the Ph groups. Reduction (Pt-black in Et_2O) of (I) yields a 2:6-dihexahydrobenzylcyclohexanone (III), m.p. 78° (oxime, m.p. $94\text{--}95^\circ$; semicarbazone, m.p. 157°), also prepared by condensing (NaOH) cyclohexanone with hexahydrobenzaldehyde, and reducing the product (Ni). Further reduction (Pt-black) of (III) yields two 2:6-dihexahydrobenzylcyclohexanols, m.p. 73° and 92° [also formed (above) from (I)] (phenylurethanes, m.p. 149° and 137° , respectively), oxidised (CrO_3) to (III). Reduction of (II) yields a third 2:6-dihexahydrobenzylcyclohexanol, m.p. $56\text{--}58^\circ$ (phenylurethane, m.p. 104°), oxidised (CrO_3) to an oily ketone (IV), giving the same oxime and semicarbazone as (III), and converted into (III) by boiling with $\text{EtOH}\text{--HCl}$. (II) yields with MgMeI a tert.-alcohol, m.p. $88\text{--}89^\circ$ [dehydrated (excess of MgMeI) to an impure hydrocarbon, ? $\text{C}_{21}\text{H}_{24}$], and with MgPhBr a tert.-alcohol, m.p. 110° . (I) with MgPhBr gives a tert.-alcohol, m.p. $110\text{--}111^\circ$ (differing from the above), unaffected by CrO_3 ; with MgMeI , (I) gives only liquid products. The oxime, m.p. 114° , of (I) is reduced (Na , isoamyl alcohol) to an amine, $\text{C}_{20}\text{H}_{25}\text{N}$ (acetate, m.p. 163°); with $\text{H}_2\text{--Pt--AcOH}$ an isomeric amine (acetate, m.p. 170°) results. The oxime, m.p. 183° , of (I) with $\text{Na} + \text{isoamyl alcohol}$ yields a third isomeride (acetate, m.p. 144°), but $\text{H}_2\text{--Pt--AcOH}$ causes hydrogenation of the Ph groups. It is concluded that (I) and (III) are *cis*- and (II) and (IV) *trans*-isomerides. The results of reducing the oximes confirm the theory that the $\text{N}\cdot\text{OH}$ is in the plane of the ring.

IX. Reduction (Ni or $\text{Na}\text{--Hg}$) of 2:5-dibenzylidenecyclopentanone yields 2:5-dibenzyl-ketones (cf. A., 1930, 474), m.p. 39° (V) and 58° (VI), either of which with NaOH , NaOEt , or HCl , or by distillation under reduced pressure, gives an equilibrium mixture of the two, the proportions varying with the reagent. Both yield the same oxime, m.p. 140° , semicarbazone, m.p. 166° , tetrahydropyrone derivative, and sec.-alcohols, m.p. 60° and 127° . Reduction (Pt-black under pressure) of (V) and (VI) yields the corresponding 2:5-dihexahydrobenzylcyclopentanones, m.p. 81° (VII) (oxime, m.p. 90°) and 73° (VIII) (oxime, m.p. 126°), respectively. 2:5-Dihexahydrobenzylidenecyclopentanone, m.p. 123° (from cyclopentanone, hexahydrobenzaldehyde, and $\text{MeOH}\text{--NaOMe}$), is reduced (H_2 , Ni, EtOH) to (VII) or to a compound (IX), m.p. $63\text{--}64^\circ$, also obtained from (VII) and $\text{Na} + \text{EtOH}$. (IX) is an approx. 45:55 solid solution of (VII) and (VIII). With MgMeI , (V) yields a tert.-alcohol, m.p. $121\text{--}122^\circ$, but (VI) yields an oil. 2-Benzylcyclopentanone, b.p. $151\text{--}5^\circ/16$ mm., obtained from α -benzyladipic acid, m.p. 118°

(? prep. from *Et* 2-benzylcyclopentanone-2-carboxylate), and Ac_2O at 155° , when benzylated, gives a product similar to that formed by benzylation of cyclohexanone.

A. Lr.

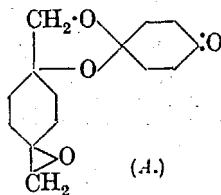
Stereochemistry of cyclanes. X. Di-*p*-methylbenzylcyclo-pentanones, -hexanones, and -heptanones. R. CORNUBERT, M. ANDRÉ, and R. JOLY. *XI*. R. CORNUBERT, C. BORREL, and A. MAUREL (Bull. Soc. chim., 1939, [v], 6, 265—270, 270—273).—X. 2:5-Di-*p*-tolylidenecyclopentanone, m.p. $235\text{--}236^\circ$, is hydrogenated (Ni formate) to 2:5-di-*p*-methylbenzylcyclopentanone (I), m.p. $67\text{--}68^\circ$, converted by 0.2N-NaOH in EtOH at room temp. into (mainly) a stereoisomeride (II), m.p. $75\text{--}76^\circ$. Either form with 0.2N-NaOH in EtOH for 36 hr., or with NaOEt for 3 days at room temp., or with HCl-EtOH for 1 week, affords an approx. 9:1 equilibrium mixture of (II) and (I); heating at \sim b.p./15—20 mm., however, gives a 1:4 mixture of (II) and (I). Hydrogenation of 2:6-di-*p*-tolylidenecyclohexanone gives 2:6-di-*p*-methylbenzylcyclohexanone (70%), m.p. 114° (III), and a stereoisomeride (5%), m.p. $85\text{--}87^\circ$ (IV). Either form, by refluxing with NaOEt-EtOH for 2 hr., or by heating at $263\text{--}265^\circ/17$ mm. for 2 hr., or by refluxing with HCl-EtOH for 4 hr., affords equilibrium mixtures of (III):(IV) of 70:25, 55:45, and 71:27 (all approx.), respectively. cycloHeptanone and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ in MeOH-NaOMe give 2:7-di-*p*-tolylidenecycloheptanone, m.p. 131° , hydrogenated (Ni formate) to 2:7-di-*p*-methylbenzylcycloheptanone, m.p. $55\text{--}56^\circ$ (V), converted by 0.2N-NaOH in EtOH at room temp. into a stereoisomeride, m.p. $66\text{--}67^\circ$ (VI). Equilibrium mixtures of (VI):(V) are obtained by 0.2N-NaOH at room temp. (4:1), by NaOEt-EtOH at room temp. (4:1) and HCl-EtOH (1 week) (3:1), or at \sim b.p./vac. (1:3).

XI. α -Benzyl- α' -methyladipic acid (cf. A., 1930, 776) is separated into two stereoisomerides, m.p. $101\text{--}105^\circ$ and $133\text{--}135^\circ$; either is cyclised by Ac_2O to the same 5-benzyl-2-methylcyclopentanone (I) [tetrahydropyrone derivative, m.p. $156\text{--}5^\circ$ (*loc. cit.*); semicarbazone, m.p. 190° , also obtained from (I) prepared by hydrogenation of 5-benzylidene-2-methylcyclopentanone (*loc. cit.*)]. *Et* 2:5-dimethylcyclopentanone-5-carboxylate (modified prep.) is converted by NaOEt at $140\text{--}150^\circ$ for 9 hr. into *Et* $\alpha\alpha'$ -dimethyladipate, b.p. $127^\circ/10$ mm., hydrolysed (EtOH-KOH) mainly to the acid, m.p. $143\text{--}5^\circ$, which is cyclised by Ac_2O to 2:5-dimethylcyclopentanone (semicarbazone, new m.p. $176\text{--}177^\circ$). A. T. P.

Reactions of $\alpha\beta$ -unsaturated cyclic aldehydes and ketones. IV. *d*-Cryptone and *trans-d*-cryptol. A. K. MACBETH and F. L. WINZOR (J.C.S., 1939, 264—266; cf. A., 1937, II, 426; 1939, II, 17).—*d*-Cryptone, $\alpha_p + 75.1^\circ$ (homogeneous), from water-fennel oil, is reduced by $\text{Al}(\text{OPr}^i)_3\text{-Pr}^i\text{OH}$ to *d*-cryptol (I), b.p. $72^\circ/2$ mm., $[\alpha]_D^{25} + 146.4^\circ$ in EtOH, purified through the *p*-nitrobenzoate, m.p. 84° , $[\alpha]_D^{25} + 174^\circ$ in CHCl_3 ; the α -naphthylurethane has m.p. $118\text{--}5^\circ$, $[\alpha]_D^{25} + 136.2^\circ$ in EtOH. (I) is a trans-epimeride, as hydrogenation (Pd-C; EtOH) gives *trans*-dihydrocryptol. (I) and $\text{K}_2\text{Cr}_2\text{O}_7\text{-aq. H}_2\text{SO}_4$ give *d*-cryptone, b.p. $78^\circ/3$ mm., $[\alpha]_D^{25} + 102^\circ$ in EtOH (semicarbazone, m.p. $187\text{--}188^\circ$, $[\alpha]_D^{25} + 33^\circ$ in CHCl_3 ; K (A., II).

2:4-dinitrophenylhydrazone, m.p. $135\text{--}136^\circ$), but is not claimed to be stereochemically pure (cf. Galloway *et al.*, A., 1937, II, 26). A. T. P.

Action of diazomethane on cyclohexane-1:4-dione. J. R. VINCENT, A. F. THOMPSON, jun., and L. T. SMITH (J. Org. Chem., 1939, 3, 603—610).—cycloHexane-1:4-dione (I) is converted by CH_2N_2 in $\text{Et}_2\text{O-MeOH}$ into 1:4-dimethylenecyclohexane dioxide (II), m.p. $106\text{--}108^\circ$, and substances (III), (IV), and (V), b.p. $65\text{--}66^\circ/2$ mm., $81\text{--}88^\circ/2$ mm., and $101\text{--}113^\circ/3$ mm., respectively. (II) does not react with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$, Fehling's solution, or decolorised fuchsin. It does not give a :CHPh derivative. Active H or CO is not present. With HCl it gives the compound, $\text{C}_8\text{H}_{14}\text{O}_2\text{Cl}_2$, m.p. $142\text{--}5\text{--}143^\circ$. It is transformed by piperidine into the substance, $\text{C}_{18}\text{H}_{34}\text{O}_2\text{N}_2$, m.p. $128\text{--}5\text{--}130^\circ$ [picrate, m.p. $222\text{--}223.5^\circ$ (decomp.)], and by very dil. AcOH at 100° into the compound, $\text{C}_8\text{H}_{16}\text{O}_4$, m.p. $199\text{--}5\text{--}201.5^\circ$. It appears to yield an aldehyde when heated with fused ZnCl_2 . (III) is $\text{C}_{13}\text{H}_{18}\text{O}_2$. It gives a semicarbazone, m.p. 202° (decomp.), an unstable phenylhydrazone, m.p. $121\text{--}127^\circ$, and a non-cryst. compound with piperidine [unstable picrate, m.p. $200\text{--}205^\circ$ (decomp.) after darkening at $\sim 190^\circ$]. When boiled with very dil. HCl it yields an org. solid, m.p. $>325^\circ$, and a viscous oil which does not react with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ or $1\text{-C}_{10}\text{H}_7\cdot\text{NCO}$. (IV) is $\text{C}_{14}\text{H}_{20}\text{O}_2$. It is converted by $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ into the disemicarbazone of (I). Further (I) separates when (IV) in Et_2O is exposed to moist air. The presence of (I) as an impurity is excluded and hence (IV) must be regarded as a compound easily cleaved by moisture to (I). CO and active H are present in (IV). Non-cryst. products are obtained from (IV) and MgPhBr , Ag_2O or CrO_3 , H_2 in presence of Raney Ni, or $\text{Al}(\text{OPr}^i)_3$, PhCHO-HCl , $\text{CH}_2(\text{CO}_2\text{H})_2\text{-C}_6\text{H}_5\text{N}$, or $\text{BuNO}_2\text{-NaOEt}$. Tars result with NH_2OH , $\text{NHPh}\cdot\text{NH}_2$, or $\text{HCl-Et}_2\text{O}$. Hydration of (IV), with or without acid catalysts, gives only oils. (IV) gives an oily product with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and does not react with $1\text{-C}_{10}\text{H}_7\cdot\text{NCO}$. With piperidine it yields the adduct, $\text{C}_{24}\text{H}_{42}\text{O}_2\text{N}_2$, m.p. $100\text{--}101^\circ$ (non-cryst. picrate). (IV) is probably (A). (V) is too unstable to permit investigation. H. W.



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Aldehyde, $\text{C}_{20}\text{H}_{34}\text{O}$ (semicarbazone, m.p. $229\text{--}230^\circ$, $[\alpha]_D^{25} + 132.8^\circ$ in CHCl_3), and ketone, $\text{C}_{18}\text{H}_{32}\text{O}$ (semicarbazone, m.p. 216° , $[\alpha]_D^{25} + 55.6^\circ$ in CHCl_3), from vitamin- D_3 .—See A., 1939, III, 292.

$\Delta^{4,5}$ -Unsaturated 3-ketones of the cyclopentano-polyhydrophenanthrene series.—See B., 1939, 326.

Partial reduction of androstenedione to testosterone. K. MIESCHER and W. H. FISCHER (Helv. Chim. Acta, 1939, 22, 158—160).—Reduction of androstenedione by $\text{Al}(\text{OBu}^t)_3$ in abs. Bu^tOH gives testosterone in 70% yield. H. W.

16-Hydroxytestosterone. A. BUTENANDT, J. SCHMIDT-THOMÉ, and T. WEISS [with, in part, D. VON DRESLER and U. MEINERTS] (Ber., 1939, 72, [B],

417—424).—Dehydroandrosterone (I) or its acetate in Et_2O is condensed with COMeEt by Na or NaNH_2 to the substance (II) ($\text{R} = \text{Me}$, $\text{R}' = \text{Et}$), m.p. 176° . The corresponding acetate, leaflets, m.p. 148° , or needles, m.p. 156° , is brominated and then ozonised in CHCl_3 ; the ozonide is transformed by Zn dust and

5—10% of *epiallopregnan-3-ol-20-one* (I), m.p. 173 — 174° (acetate, m.p. 139 — 140°), which is purified by adsorption on Al_2O_3 . (I) is devoid of androgenic activity. W. McC.

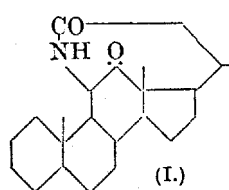
Preparation of progesterone and neoprogesterone from dehydroandrosterone. K. MIESCHER and H. KÄGI (Helv. Chim. Acta, 1939, 22, 184—195).—Addition of $\text{CMeCl}_2 \cdot \text{CO}_2\text{Et}$ in Et_2O to a mixture of *t*-dehydroandrosterone acetate and Mg-Hg in Et_2O , removal of secondary volatile products by steam distillation, and treatment of the resultant product (A), with MeOH-NaOH give *Et* Δ^5 -3*t*-acetoxy-17:20-oxidobisnorcholenate, m.p. 150 — 151° . Alkaline hydrolysis of (A) gives a mixture (I) of acids from which 3-*t*-hydroxy-17:20-oxidobisnorcholenic acid (II), m.p. 186 — 187° (*Me* ester, m.p. 150 — 151° , $[\alpha]_D^{25} -123^\circ$ in EtOH , and its acetate, m.p. 172 — 174° , $[\alpha]_D^{25} -121^\circ$ in EtOH), is separated. The mother-liquors from (II) contain an isomeric acid B (III), $\text{C}_{22}\text{H}_{32}\text{O}_4$, m.p. 248° (decomp.) [*Me* ester (+ H_2O), m.p. 73 — 74° , $[\alpha]_D^{25} -160^\circ$ in EtOH , and its acetate, m.p. 175 — 176° , $[\alpha]_D^{25} -146^\circ$ in EtOH]. Direct methylation of (I) followed by acetylation and chromatography with flordin leads to the isolation of the acetates of the *Me* esters of acids C and D, $\text{C}_{25}\text{H}_{36}\text{O}_5$, m.p. 153 — 154° , $[\alpha]_D^{25} -81^\circ$ in EtOH , and m.p. 189° , $[\alpha]_D^{25} -49^\circ$ in EtOH . In quinoline at 200° (I) gives (III) (which is decarboxylated with great difficulty) (unexamined), non-ketonic material, and a mixture of ketones (as acetates). This is separated chromatographically (Al_2O_3 or flordin) into pregnenolone acetate, m.p. 148.5 — 149.5° , $[\alpha]_D^{25} +18^\circ$ in EtOH , and neopregnenolone acetate, m.p. 178 — 179° , $[\alpha]_D^{25} -114^\circ$ in EtOH , hydrolysed to neopregnenolone (IV), m.p. 223 — 224° , $[\alpha]_D^{25} -124^\circ$ in EtOH . Bromination oxidation, and debromination of crude (IV) leads to neoprogesterone, m.p. 217 — 218° , $[\alpha]_D^{25} +48^\circ$ in CHCl_3 , and progesterone. H. W.

AcOH into the carboxylic acid (III), m.p. 251° (decomp.) (softens 235°) (anhydride, m.p. 186°), and 3-acetoxy-androstenedione (IV) (+ H_2O), m.p. 192° [oxime, m.p. 244° (decomp.)], hydrolysed to 3-hydroxyandrostenedione, m.p. 197° (diacetate, m.p. 123°). (IV) is hydrogenated to 3-acetoxyandrostene-16:17-diol, m.p. 179° , transformed by cold $\text{AcOH-C}_5\text{H}_5\text{N}$ into the triacetate, m.p. 224 — 226° , and hydrolysed by 4% KOH-MeOH to androstene-3:16:17-triol (V), m.p. 273 — 275° . COMe_2 containing 1% of HCl transforms (V) at room temp. into the CMe_2 ether, m.p. 163 — 164° , oxidised by $\text{Al(OPr}^i)_3$ in cyclohexanone and PhMe to 16-hydroxytestosterone CMe_2 ether, m.p. 183 — 184° , which is hydrolysed by aq. AcOH in boiling dioxan to 16-hydroxytestosterone (VI), m.p. 172 — 173° (diacetate, m.p. 199°). The physiological action of (V) shows that the introduction of OH at C_{16} causes a marked weakening of the male hormone action whereas that of (VI) proves that the introduction produces enhanced oestrogenic activity. COMe_2 and (I) condense to the isopropylidene derivative [cf. (II), $\text{R} = \text{R}' = \text{Me}$], m.p. 223° (acetate, m.p. 189°). H. W.

Saponins and sterols. V. Synthesis of 17-methylandrosten-17-ol-3-one (17-methyltestosterone). VI. Oxidation of dibromo[dihydro]cholesteryl acetate. Synthesis of pregnen-3-ol-20-one. K. FUJII and T. MATSUKAWA (J. Pharm. Soc. Japan, 1935, 55, 1333—1336; 1936, 56, 158—161).—V. 17-Methyl- Δ^5 -androsten-3:17-diol, m.p. 195 — 196° [from *trans*-dehydroandrosterone (I) and MeMgI], was brominated, oxidised ($\text{CrO}_3\text{-AcOH}$), and debrominated (Zn) to yield 17-methyltestosterone (17-methyl- Δ^5 -androsten-17-ol-3-one), m.p. 155 — 156° (corr.).

VI. On repeating the prep. of (I) from dibromodihydrocholesteryl acetate by oxidation, pregnen-3-ol-20-one acetate, m.p. 147 — 148° (corr.) [semicarbazone, m.p. ? 265° (corr.)], was isolated, hydrolysis yielding pregnen-3-ol-20-one (II), m.p. 186° . The synthesis of (II) from 3-hydroxycholesterol acid is proposed. CH. ABS. (c)

Supposed androgenic action of epiallopregnan-3-ol-20-one. A. BUTENANDT and A. HEUSNER (Z. physiol. Chem., 1938, 256, 236—242; cf. Marker *et al.*, A., 1937, II, 250).—Pregnenolone (A., 1934, 1268) in AcOH with Pt-H_2 to saturation gives a mixture of allopregnane-3:20-diols which with $\text{CrO}_3\text{-AcOH}$ at room temp. yields allopregnanedione, reduced (Ni-H_2 , EtOH) to a mixture of allopregnanolone (separated by pptn. with digitonin) together with



amino-12(11)-ketocholesterol acid, isolated as the hydriodide (+ H_2O) (II), m.p. $\sim 285^\circ$ (corr.; decomp.). Reductive removal of O vicinal to NH_2 could not be effected. (II) is converted by CH_2N_2 into Me11(12)-amino-12(11)-ketocholesterolanate (III) characterised as the hydrochloride, m.p. 235° (decomp.) after softening $\sim 230^\circ$, or the *Ac* derivative, m.p. 214 — 216° . The proof that (I) is merely hydrolysed by HI is afforded by the observation that (III) is transformed into (I) in good yield by the protracted action of MeOH at 130° . In harmony with the present formulation (I) is unchanged by the protracted action of CrO_3 in AcOH at room temp. Me 12-keto- Δ^5 -11-cholesterol is unaffected by H_2 at room temp. in presence of $\text{PtO}_2\text{-MeOH-AcOH}$. With Raney Ni and H_2 at $100^\circ/140$ atm. it gives a non-cryst. product, oxidised

essentially to Me 12-ketocholanate. All m.p. are corr. H. W.

Catalytic hydrogenation of organic compounds with carbon monoxide. O. NEUNHOEFFER and W. PELZ (Ber., 1939, 72, [B], 433—439).—The catalyst is prepared by pptg. Pd from aq. PdCl_2 by H_2 on a suitable carrier, preferably active C (BaSO_4 and sugar C can also be used). During the action the gases are circulated through a system containing conc. aq. KOH to remove the CO_2 produced, small traces of which very appreciably restrict hydrogenation. In H_2O the hydrogenation is slow and succeeds best with 3—10% HCl. Usually there is a distinct induction period. Hydrogenation with CO cannot be applied to all substances which absorb H_2 . $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is very slowly reduced to $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ but reduction of PhNO_2 or cyclohexene does not occur. Quinones are very suitable acceptors. p -Benzoquinone (I) acts most rapidly and is followed in order of decreasing velocity by toluquinone (II), thymoquinone (III), phenanthraquinone (IV), and 2 : 5-dihydroxy- p -benzoquinone (V). Anthraquinone (VI) does not give a certain result, whilst 2-hydroxynaphthaquinone is not attacked. Pd does not cause reduction of (I) by H_2 . This change proceeds rapidly in the presence of a Pt catalyst; there is no distinct pause at the quinol stage and reaction proceeds to the formation of cyclohexanol. Toluquinol is not formed from (II) in presence of Pd and H_2 ; (III) reacts very slowly and incompletely whereas the change occurs better with (IV), (V), and (VI). The mechanism of hydrogenation by CO is discussed. H. W.

Oxidation-reduction potentials of substituted quinoneanils and indoanilines. L. F. FIESER and H. T. THOMPSON (J. Amer. Chem. Soc., 1939, 61, 376—383).—Studies with 3-substituted 1 : 4-quinoneanils show that substituents exert their effect on both oxidant and reductant. 1 : 4-Naphthaquinoneanil (E_0 0.532 v.), m.p. 102°, with Zn dust and NaOAc in Ac_2O gives *phenyl-4-acetoxy-1-naphthylamine*, m.p. 135°. $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\alpha$ (modified prep.), m.p. 85° (lit. 91°), and HgO in C_6H_6 give *p-benzoquinone-2' : 3'-benzanil* (E_0 0.678 v.), m.p. 138°, reduced to *p-acetoxyphenyl- α -naphthylamine*, m.p. 135°. Phenolblue (E_0 0.650 v.), prepared from PhOH , NaOAc, and NaOH by NaOCl and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{HCl}$ at 0° to -5°, and reduced to 4-dimethylamino-4'-hydroxydiphenylamine hydrochloride, is considered to be $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot p$ over the whole p_H range studied. 2-Methyl- NN -dimethylindoaniline [2-methyl-1 : 4-benzoquinone-4- p -dimethylaminoanil] (similarly prepared) (E_0 0.6081 v.), new m.p. 127°, gives 4'-dimethylamino-4-hydroxy-3-methyldiphenylamine hydrochloride. 3-Methyl- NN -dimethylindoaniline (E_0 0.6343 v.), new m.p. 121°, gives 4'-dimethylamino-4-hydroxy-2-methyldiphenylamine, m.p. 121—122° (decomp.) (hydrochloride). 2 : 1 : 5- $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\text{Me}\cdot\text{NMe}_2$ gives 2'-methyl- NN -dimethylindoaniline (E_0 0.6425 v.), m.p. 113—114°, reduced to 4-dimethylamino-4'-hydroxy-2-methyldiphenylamine hydrochloride. 2 : 4 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{N}_2\text{Cl}$ and $o\text{-C}_6\text{H}_4\cdot\text{Me}\cdot\text{NMe}_2$ give a dye (Na salt), reduction of which gives only a triazole, but the dye,

$p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{NMe}_2\cdot 1 : 3 : 4$, m.p. 122°, with SnCl_2 gives 2 : 1 : 5- $\text{NMe}_2\cdot\text{C}_6\text{H}_3\cdot\text{Me}\cdot\text{NH}_2$, b.p. 253—255°/762 mm., new m.p. 45—46° (dihydrochloride; Ac derivative, m.p. 96°), which, however, gives no indoaniline. $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ gives crude 3-methoxy- NN -dimethylindoaniline (E_0 0.5905 v.) and thence 4'-dimethylamino-4-hydroxy-2-methoxydiphenylamine, m.p. 137°. The hydrochloride of 4-nitroso- NN -dimethyl- m -anisidine (prep. by HNO_2), m.p. 131°, gives (SnCl_2) the 4- NH_2 -derivative, b.p. 130—131°/4 mm. (dihydrochloride), which affords 2'-methoxy- NN -dimethylindoaniline (E_0 0.6355 v.) and thence 4'-dimethylamino-4-hydroxy-2'-methoxydiphenylamine hydrochloride. $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ (prep. from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$) affords (crude) 3-chloro- NN -dimethylindoaniline (E_0 0.6888 v.) and thence 2-chloro-4'-dimethylamino-4-hydroxydiphenylamine hydrochloride. $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NMe}_2$, b.p. 239—240° (picrate, m.p. 145°), prepared from NPhMe_2 by way of the NO_2 , m.p. 60°, and NH_2 -derivative, b.p. 128—129°/7 mm., gives the NO-derivative, m.p. 136° (decomp.), and thence 2-chloro-4-dimethylaminoaniline, b.p. 124—125°/3 mm., m.p. 40—41° (hydrochloride; Ac derivative, m.p. 117°), which yields (crude) 2'-chloro- NN -dimethylindoaniline (E_0 0.6683 v.) and thence 2-chloro-4-dimethylamino-4'-hydroxydiphenylamine hydrochloride. ar -Tetrahydro- α -naphthol gives (crude) 2 : 3-tetramethylene- NN -dimethylindoaniline (E_0 0.5828 v.) and thence p -dimethylaminophenyl-4'-hydroxy-5' : 6' : 7' : 8'-tetrahydro-1'-naphthylamine, m.p. 158°. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NMe}_2$ is reduced by $\text{Na}\cdot\text{C}_6\text{H}_{11}\cdot\text{OH}$ to the H_4 -derivative, which with $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ gives a dye, reduced to 4-dimethylamino-5 : 6 : 7 : 8-tetrahydro-1-naphthylamine, b.p. 312° (dihydrochloride; Ac derivative, m.p. 172.5°), which, however, yields no indoaniline. R. S. C.

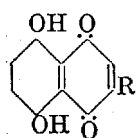
Reaction of thiol compounds with quinones. J. M. SNELL and A. WEISSBERGER (J. Amer. Chem. Soc., 1939, 61, 450—453).—1 mol. each of $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ (I) and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II) in aq. EtOH give a product, dehydrated at 150° to *quinol-2-thiolacetolactone* (III), m.p. 169—171°; (I) (2 mols.) and (II) (1 mol.) give 1 : 4-benzoquinone-2-thiolacetic acid, m.p. 157—158° (decomp.) (and 1 mol. of quinol), reduced (Zn-AcOH) to (III). $\text{SH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ and (I) (2 mols.) give 1 : 4-benzoquinone-2-thiolacetanilide, m.p. 175—176° (lit. 165—166°), and PhSH gives 2-phenylthiol-1 : 4-benzoquinone, m.p. 110—112°, reduced by Zn dust in AcOH to a syrup, which with Ac_2O and a little H_2SO_4 yields 2-phenylthiolquinol diacetate, m.p. 84—85°. EtSH and (I) at 100° give 2 : 5-diethylthiol-1 : 4-benzoquinone, m.p. 158—159°; Récséi's so-called 1 : 1-diethanesulphonyl- $\Delta^{2:5}$ -hexadien-4-one (A., 1927, 1079) has not the composition stated. $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ and (I) in EtOH give 1 : 4-benzoquinone-2 : 5-di(thiolpropionic acid), m.p. ~240° (decomp.), and -2-thiolpropionic acid, m.p. 165—166° (reduced by Zn-AcOH to β -2 : 5-dihydroxyphenylthiolpropionic acid, m.p. 121—123°). ψ -Cumoquinone (IV) and (II) in EtOH give 2 : 5-dihydroxy-3 : 4 : 6-trimethylphenylthiolacetic acid, double m.p. 142° (decomp.) and ~190°, oxidised by $\text{FeCl}_3\text{-HCl}$ to 3 : 5 : 6-trimethyl-1 : 4-benzoquinone-2-thiolacetic acid, softens at 123°, m.p. 126—127°. $n\text{-C}_{18}\text{H}_{37}\cdot\text{S}(\text{NH}_2)\cdot\text{NH}$, m.p. 83—85°, gives $n\text{-C}_{18}\text{H}_{37}\cdot\text{SH}$, b.p. 165—170°/1 mm., which with (IV) gives 3 : 5 : 6-

trimethyl-2-n-octadecylthiol-1:4-benzoquinone, m.p. 71—73°, reduced to 3:5:6-*trimethyl-2-n-octadecylthiol-quinol*, m.p. 76—77°. In 80% EtOH duroquinone and (II) give duroquinol if the reaction mixture is slightly alkaline (Na_2CO_3); otherwise no reaction occurs. PhSH and *p*-xyloquinone give 2-*phenylthiol-3:5-dimethyl-1:4-benzoquinone*, m.p. 106—107°. Addition of RSH to quinones thus gives quinol derivatives, which may be oxidised to the quinone derivatives with simultaneous reduction of part of the original quinone to quinol. R. S. C.

4-Alkyl derivatives of 1:2-naphthaquinone. L. F. FIESER and C. K. BRADSHAW (J. Amer. Chem. Soc., 1939, 61, 417—423).—4-Alkyl-1:2-naphthaquinones react generally as true quinones. 1:4- $\text{C}_{10}\text{H}_7\text{Me}\cdot\text{SO}_3\text{K}$ (modified prep. in 58% yield from 1- $\text{C}_{10}\text{H}_7\text{Me}$) gives 1:4- $\text{C}_{10}\text{H}_7\text{Me}\cdot\text{OH}$, which, by coupling with *p*- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$, followed by reduction, affords 52% of 2-*amino-4-methyl-1-naphthol hydrochloride*, oxidised by $\text{FeCl}_3\text{--HCl}$ to 4-*methyl-1:2-naphthaquinone* (I) (89%), m.p. 109° (decomp.). (I) is unstable in air and in hot MeOH, has E_0 0.531 v. in EtOH, and with Zn dust in $\text{Ac}_2\text{O--AcOH}$ gives 3:4-*diacetoxy-1-methylnaphthalene*, m.p. 124.5—125.5°; it is insol. in alkali and bears no relation to the compound of Dean *et al.* (A., 1916, i, 555), which was believed to be the enolic form, but is probably a multimol. condensation product. With Cl_2 in AcOH (I) gives the 3-*Cl*-derivative, decomp. 150—160° [oxidised by KMnO_4 to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$], the Cl of which does not react with AgOAc or $\text{CHNa}(\text{CO}_2\text{Et})_2$. 1:4- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{COPh}$ (improved prep.), m.p. 81—82°, with H_2 + Cu—Ba chromite at 175°/167 atm. (not Zn—Hg—HCl) gives 1:4- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\text{Ph}$ (84—86%), m.p. 83—84°, converted by HBr--AcOH into 1:4- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\text{Ph}$, m.p. 122.5—123.5°, and thence (*p*- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$, $\text{Na}_2\text{S}_2\text{O}_4$) into the 2- NH_2 -derivative, which with $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ gives 4-*benzyl-1:2-naphthaquinone* (II), softens at ~130°, m.p. 148° (decomp.). (II) is stable, gives a *phenazine* derivative, m.p. 195.5—196° (corr.), has E_0 0.562 v., and yields 3:4-*diacetoxy-1-benzyl-naphthalene*, m.p. 96—96.5° (corr.). Et_2 naphtha-1:2-quinone-4-malonate (III) [modified prep.; cf. Sachs *et al.*, A., 1905, i, 909], m.p. 105—106°, with $\text{Ac}_2\text{O--NaOAc}$ or $\text{Ac}_2\text{O--H}_2\text{SO}_4$ gives the *acetate*, m.p. 93—94°, of the isomeric 2-hydroxy-1:4-quinone-4-methide, but normally exists, and in other reactions behaves, as (III). Thus with $\text{Na}_2\text{S}_2\text{O}_4$ it gives Et_2 3:4-*dihydroxy-1-naphthyl-malonate*, m.p. 132° (decomp.), the Ac_2 derivative [prep. from (III) by $\text{Ac}_2\text{O--AcOH--Zn}$ dust], m.p. 95—96°, of which with HCl--AcOH , followed by Ac_2O and a trace of H_2SO_4 , gives 3:4-*diacetoxy-1-naphthylacetic acid*, m.p. 158—159° (could not be decarboxylated; decomp. with Cu). (III) gives a *phenazine* derivative, m.p. 164—165°, converted by hot 10% KOH into 3-carboxymethyl-1:2-benzphenazine, m.p. 168—172°, converted by Cu—bronze in quinoline at 140—190° into CO_2 and 3-methyl-1:2-benzphenazine, m.p. 174°, which is also obtained from (I) and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. With $(\text{CH}_3)_2\text{CMe}_2$ in EtOH at 100° (II) and (III) give poor yields of 12-*benzyl-2:3-dimethyl-*, m.p. 179—179.5° (corr.), and 2:3-*dimethyl-12-dicarbethoxymethyl-*, m.p. 127—128° (corr.), -1:4:11:12-*tetrahydrophenanthra-*

9:10-*quinone*, respectively. With NH_2Ph in EtOH at 100° (I), (II), and (III) lose the 4-substituent, giving 2-anilino-1:4-naphthaquinone-4-anil. With Ac_2O and a drop of conc. H_2SO_4 (I) gives an abnormal *triacetate*, $\text{C}_{17}\text{H}_{16}\text{O}_6$, m.p. 101—102°, hydrolysed by cold, aq. alkali and oxidised by KMnO_4 to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$; (II) gives similarly or with $\text{Ac}_2\text{O--NaOAc}$ a *triacetate*, $\text{C}_{23}\text{H}_{30}\text{O}_6$, m.p. 139.5—140°. 3-Chloro-1:2-naphthaquinone with $\text{Ac}_2\text{O--H}_2\text{SO}_4$ gives 3-chloro-1:2:4-*triacetoxynaphthalene*, m.p. 172—173°, but the 4-chloroquinone is unchanged. R. S. C.

Constitution of shikonin. II. Synthesis of alkyl derivatives of naphthazarin, naphthapurpurin, and related compounds. C. KURODA and M. WADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 34, 1740—1761; cf. A., 1937, II, 66, 344).—Naphthazarin is prepared from 1:5- $\text{C}_{10}\text{H}_6(\text{NO}_2)_2$, 18% oleum, and S at 60°, or from quinol, maleic anhydride, and $\text{AlCl}_3\text{--NaCl}$ at 300°. *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OAcyl}$ with $\text{AlCl}_3\text{--NaCl}$ at 200° give 2-acylquinols (A., m.p. 202°, *propionyl*, m.p. 97°, *n*-butyryl, m.p. 175°), reduced (Clemmensen) to the 2-alkylquinols (*Et*, m.p. 112°, *Pr*, m.p. 88°, *isoamyl*, m.p. 101°), which with maleic anhydride and $\text{AlCl}_3\text{--NaCl}$ yield 2-alkyl-naphthazarins (*Pr*, m.p. 97°). 1:2:4- $\text{C}_6\text{H}_3(\text{OH})_3$ with maleic anhydride and $\text{AlCl}_3\text{--NaCl}$ gives naphthapurpurin. Similarly 3-methoxy-2-methylquinol (prepared thus: *o*-cresol \rightarrow 3:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe} \rightarrow \text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe} \rightarrow$ 3-methoxy-2-methyl-benzoquinone and -quinol) yields 5:7:8-trihydroxy-6-methyl-1:4-naphthaquinone, m.p. 193°, identical with the known compound. 1:2:4- $\text{C}_6\text{H}_3(\text{OH})_3$ with citraconic anhydride and $\text{AlCl}_3\text{--NaCl}$ yields 5:6(or 7):8-trihydroxy-2-methyl-1:4-naphthaquinone, m.p. 202°, identical with that obtained from methyl-naphthazarin [m.p. 202°, wrongly reported as 192° (A., 1937, II, 344)]. Hence the compounds previously reported (*loc. cit.*) as 3:5:8-trihydroxy-2-*isohexyl*- and -ethyl-naphthaquinone are really 5:6(or 7):8-trihydroxy-2-alkyl-compounds. Since shikonin is laevo-rotatory, being enantiomeric with alkannin, and resembles in properties the alkyl-naphthazarins rather than -purpurins, it is given the formula (I) [R = $\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}(\text{Me})_2$]. Further details and analyses of previous work (*loc. cit.*) are given. A. Li.



Oxidation of alkylanthracenes, alkylanthraquinones, and their derivatives. I. Oxidation with chromic anhydride of 2-methylantraquinone to anthraquinone-2-carboxylic acid. II. Influence of water on the oxidation of 2-methylantraquinone to anthraquinone-2-carboxylic acid by chromic anhydride. M. A. ILJINSKI, L. G. GINDIN, and V. A. KASAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 555—558, 559—560).—I. Oxidation of 2-methylantraquinone (I) with CrO_3 in glacial AcOH at 70° gives anthraquinone-2-carboxylic acid (II) in 96% yield.

II. The presence of small quantities of H_2O in the AcOH drastically reduces the yield of (II) from the oxidation of (I) with AcOH--CrO_3 . J. D. R.

Constitution and synthesis of phoenicin, the pigment of *Penicillium phoeniceum*. T. POSTERNAK (Arch. Sci. phys. nat., 1938, [v], 20, Suppl., 63—65).—Phoenicin (Friedheim, Compt. rend. Soc. Biol., 1933, 112, 1030), $C_{14}H_{10}O_6$, m.p. 231°, is shown to be 2:2'-dihydroxy-4:4'-dimethyldiphenyl-3:6:3':6'-diquinone. It is dibasic, gives yellowish-red solutions at p_H 1.6—3.5 and reddish-violet solutions at p_H 4.9—6.0, liberates 4 I from HI, gives a diquinol, m.p. 247° [hexa-acetate (I), m.p. 202—203°], with CrO_3 yields 2 AcOH, with dehydrating agents loses H_2O to give a dibenzofuran derivative, and with 2 mols. of cyclopentadiene gives an adduct, $C_{24}H_{22}O_6$, m.p. 181°. 4:4'-Dimethyldiphenyl-3:6:3':6'-diquinone (ditoluquinone) and $Ac_2O-H_2SO_4$ yield (I) and a small amount of an isomeride, m.p. 181—182°.

R. S. C.

Catalytic hydrogenation of α - and β -ionone. J. KANDEL (Ann. Chim., 1939, [xi], 11, 73—142).—Mainly an account of work already reported (A., 1937, II, 108, 415; 1938, II, 96). Tetrahydroionol with $K_2Cr_2O_7-H_2SO_4$ gives tetrahydroionone [semicarbazone, m.p. 194—195° (corr.); block], 182° (corr.; tube). α - and β -Ionol, respectively, and SiO_2 gel at 300° give 2:4:4-trimethyl-3- (α -ionene) and 1:3:3-trimethyl-2- $\Delta^{\alpha\gamma}$ -butadienyl- Δ^1 -cyclohexene (β -ionene), previously (loc. cit., 1938) erroneously named 3- $\beta\delta\delta$ - and 2- $\alpha\gamma\gamma$ -trimethylbutadienylcyclohexene, respectively. Tetrahydroionyl 3:5-dinitrobenzoate melts at 75° (block).

R. S. C.

Bitter constituents of navel and Valencia oranges.—See A., 1939, III, 343.

Citronellal-terpene. II. Structure of the new terpene "menogene." H. OTSUKI (J. Chem. Soc. Japan, 1936, 57, 415—423; cf. A., 1937, II, 200).—Menogene (I), which occurs together with isomeric α -terpinene in the distillate from citronellal and H_2SO_4 , is structurally related to $\Delta^{2:4(8)}$ -p-menthadiene. It gives with Na orange-red colour reactions and on distillation (but not with KOH in EtOH) COME₂ and two fractions, b.p. 100—130° and 184—186°. (I) and maleic anhydride in C_6H_6 or Et_2O and then with MeOH gives an unsaturated adduct, $C_{14}H_{18}O_3 \cdot 5H_2O$, m.p. 205—208°, softening at 195° (additive product with Br, m.p. 282—285°). Hydrogenation of (I) (PdO) gives p-menthane.

CH. ABS. (c)

Spatial isomerism in the fenchol series. H. SCHMIDT and L. SCHULZ (Schimmel & Co., Ann. Rep., 1935, 93—95).— β -Fenchol (I), m.p. 3—4°, b.p. 200.5°/750 mm. (phenylurethane, m.p. 90—90.5°; H phthalate, m.p. 153—153.5°), bears the same relation to fenchol (II) as isoborneol to borneol; (I) and (II) differ markedly in odour but yield the same fenchone on oxidation. Properties of all the isomeric fenchols are summarised.

CH. ABS. (c)

Monochlorinated derivatives of pinane. G. BONNET (Bull. Inst. Pin, 1938, 217—232, 241—256; 1939, 1—12).—d-Pinane (I), b.p. 166°, $[\alpha]_D^{25} +24.97^\circ$, $[\alpha]_D^{25} +28.50^\circ$, is obtained by hydrogenation (Adams) of d-pinene in EtOH, and purified from any unchanged material by conc. H_2SO_4 or by a second hydrogenation; the use of $KMnO_4$ is unsuccessful. l-Pinane (II) is obtained similarly from a mixture of pinene and

nopinene (III) or from (III). (I) and (II) are scarcely attacked by Cl_2 in diffused light in the absence of catalyst but the action occurs readily in bright light. Under these conditions (I) yields l-2-chloropinane (IV), b.p. 57°/2.5 mm., $[\alpha]_D^{25} -5.46^\circ$, $[\alpha]_D^{25} -5.95^\circ$, d-7-chloropinane (V), b.p. 66°/2.5 mm., $[\alpha]_D^{25} +9.77^\circ$, $[\alpha]_D^{25} +10.75^\circ$, and dichloropinane, b.p. 102°/2.5 mm., $[\alpha]_D^{25} -11.07^\circ$, $[\alpha]_D^{25} -12.54^\circ$, the Raman spectra of which are recorded. (IV) is unaffected by Na and abs. EtOH or by Al-Hg and Et_2O or 96% EtOH, but is converted by Zn-Cu into (I). Replacement of Cl by OH in (IV) cannot be effected by alkali, alkaline-earth, or Ag hydroxides since these reagents essentially cause withdrawal of HCl, as does $AgOAc$. Treatment of (IV) in Et_2O by Mg followed by O_2 and H_2O leads to cis-l-pinocampheol, m.p. 58—59° (H phthalate, m.p. 109—110°), oxidised by CrO_3 in AcOH to d-pinocampheol, b.p. 59°/3 mm., 211—212°/760 mm., $[\alpha]_D^{25} +20.28^\circ$, $[\alpha]_D^{25} +24.11^\circ$. dl-2-Chloropinane (obtained by mixing equal wts. of the optical isomerides) is similarly transformed into dl-pinocampheol, m.p. 41—43°, and dl-pinocampheol, b.p. 59—60°/3 mm., 210—212°/770 mm. (semicarbazone, m.p. 207°), oxidised by $KMnO_4$ to dl-pinonic acid. Boiling KOH-EtOH is without action on (IV), from which HCl is very incompletely removed by NaOMe. (IV) is converted by KOPh at 150° into α -pinene, probably containing a little δ -pinene. (V) is not reduced satisfactorily by Na-EtOH or by Al-Hg but is converted by Zn-Cu into (I). The successive action of Mg in Et_2O , O_2 , and H_2O on (V) leads to cis-myrtanol, b.p. 81—82°/3 mm., $[\alpha]_D^{25} +12.67^\circ$, $[\alpha]_D^{25} +14.70^\circ$ (H phthalate, m.p. 120°), oxidised to cis-myrtanal. Withdrawal of HCl from (V) gives principally (III), with smaller amounts of α - and probably δ -pinene, identified by the Raman spectrum and by conversion into nopinone (semicarbazone, m.p. 187°). Chlorination of (I) in daylight at 50° occurs very slowly. At 75° more (I) remains unattacked and less (IV) is produced whereas the proportions of (V) and polychloro-derivatives are essentially the same as when chlorination is effected at room temp. in bright light. At 100°, 44% of the material is unchanged, 23% of Cl_1 - and 33% of polychloro-derivatives are formed. With the boiling material the proportion of polychloro- is somewhat increased at the expense of the Cl_1 -derivative but there is evidence of decomp. The course of chlorination of (I) in presence of PCl_5 is very similar to that under the influence of intense light or higher temp. With S_2Cl_2 , I, or $FeCl_3$ the proportion of unchanged material and polychloro-compounds is greatly increased and that of Cl_1 -derivatives is diminished. At room temp., in daylight and in presence of I the Cl_1 -compounds consist mainly of bornyl chloride (VI) with some (IV) and possibly (V). The proportion of (VI) appears somewhat increased if action takes place in the dark or at raised temp. (VI) is identified by conversion into camphene, isobornyl formate, and isoborneol.

H. W.

Action of acetic acid on α -pinene in presence of boron trioxide. M. IMOTO (J. Soc. Chem. Ind. Japan, 1938, 41, 375—376n).— α -Pinene and AcOH of various grades in presence of B_2O_3 at 100—120° gives 45% of an ester hydrolysed to borneol, iso-

borneol, and fenchyl alcohol. Other terpenes are also formed.

E. W. W.

Acidic oxidation products of lupenyl esters : addition of hydrogen chloride to lupeol. A. DUERDEN, I. M. HEILBRON, W. McMECKING, and F. S. SPRING (J.C.S., 1939, 322—324).—Ozonolysis of lupenyl acetate (cf. A., 1938, II, 195) gives the acetate-acid A ($C_{30}H_{50}O_4$ or $C_{31}H_{50}O_4$), m.p. 272° (Me ester, m.p. 232—234°), hydrolysed to the OH-acid A, m.p. 262—264°, also obtained by ozonolysis of lupenyl benzoate. Oxidation of lupenyl acetate with CrO_3 affords the acetate-acid B, m.p. 296° (cf. Ruzicka *et al.*, *ibid.*) (acetate-anhydride, m.p. 195—197°, remelts 277—284°), and similar oxidation of the benzoate yields the benzoate-acid, m.p. 320—322°. Lupcol and HCl form *lupeol hydrochloride* (I) m.p. 195—196° [α_D^{20} -10.3° in $CHCl_3$, which with $AgOAc$ gives lupenyl acetate and with $NPhMe_3$ affords *isolupenyl acetate*, m.p. 269—270°, [α_D^{20} +25.26° in $CHCl_3$. The mother-liquors from the prep. of (I) with Ac_2O yield an acetate, m.p. 231—232°, not identical with β -amyrenyl acetate.

F. R. S.

Structure of origanene. I. A. J. BIRCH (J. Proc. Roy. Soc. New South Wales, 1938, 74, 330—335).—Careful fractionation of technical α -phellandrene (from *Eucalyptus dives*) and treatment of the product with maleic anhydride gives what appears to be a reasonably pure origanene (I), b.p. 155—160°, α_D^{25} +12.5°, the physical consts. of which differ somewhat from those recorded by Pickles (J.C.S., 1908, 93, 862) so that it is improbable that (I) is a monocyclic terpene as postulated by him. Titration with Br in glacial AcOH indicates the presence of one double linking so that, considered along with the analytical results, it is very probable that (I) is a dicyclic terpene; this supposition agrees well with the observed physical consts. Pickles' observation of the formation of terpin hydrate or *p*-cymene from (I) could not be confirmed. The nitrosochloride (II) and the nitrolpiperidide are optically inactive in $CHCl_3$. Oxidation of (I) with H_2O_2 gives only liquid products from which $(CH_2CO_2H)_2$ could not be extracted whilst dil. aq. $KMnO_4$ affords a small amount of neutral ketonic material with $H_2C_2O_4$ and liquid acids which do not react with 2:4-(NO_2) $_2$ $C_6H_3 \cdot NH \cdot NH_2$. With EtOH-KOH (II) gives only liquid products whereas C_5H_5N yields a small amount of cryst. material, m.p. 151°, possibly a previously unknown oxime. The following derivatives are described: *nitrolmorpholide*, m.p. 190°; *nitrolpiperidide*, m.p. 198°; *nitrolbenzylamide*, m.p. 106°; *nitroldiethylamide*, m.p. 140°; *nitroldimethylamide*, m.p. 178°; *nitroldiisobutylamide*, m.p. 120°; *nitrol- α -phenylethylamide*, m.p. 161°. H. W.

Constitution of gmelinol. I. A. J. BIRCH and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 74, 391—405; cf. Smith, A., 1913, i, 1057).—Extraction of the wood of *Gmelina Leichhardtii* ("colonial beech") with boiling H_2O gives gmelinol (I), m.p. 124° after softening at 122°, which is now shown by analyses and determinations of mol. wt. in freezing C_6H_6 to be $C_{21}H_{34}O_7$. It contains 4 OMe and, with some difficulty, yields a *phenylurethane*, m.p. 189°, reconverted by boiling KOH-EtOH into (I). Since (I) does not give any ketonic compound

when oxidised, the OH is probably *tert*. (I) distils almost unchanged at about 330°/20 mm. but under atm. pressure it breaks down into veratric acid (II), veratraldehyde (III), and, mainly, homoveratrole. (I) is readily converted by mineral acids into a dark brown resin whereas boiling 20% HCO_2H transforms it into *isogmelinol* (IV), m.p. 147°, which is dextro-rotatory in $CHCl_3$. The yield of homogeneous (II) obtained by oxidation of (I) with $KMnO_4$ strongly suggests the presence of two veratryl residues whilst a somewhat lower yield is obtained by the similar oxidation of (IV). (I) is oxidised by HNO_3 to 4:5-dinitroveratrole in amount somewhat < that required for one veratryl residue. Further support of the hypothesis that (I) contains two veratryl residues is found in the observation that (II) is the sole isolable product of the oxidation with $KMnO_4$. Oxidation of (I) in glacial AcOH with a deficiency of CrO_3 gives (III) and unchanged (I). Fuming HNO_3 converts (I) in glacial AcOH at room temp. into *dinitro-gmelinol*, $C_{21}H_{12}O_7(NO_2)_2$, m.p. 190°, which is optically active, insensitive to the action of aq. or alcoholic acids, and resistant to oxidation by $KMnO_4$. Prolonged treatment of it with $PhNCO$ results in a tar. It is indifferent towards 2:4-(NO_2) $_2$ $C_6H_3 \cdot NH \cdot NH_2$. Controlled oxidation by CrO_3 in AcOH leads almost certainly to 6-nitroveratraldehyde [2:4-dinitrophenyl-hydraxone, m.p. 260° (decomp.)]. *Dinitroisogmelinol*, m.p. 235°, is obtained similarly from (IV). Bromination of (I) in C_6H_6 containing C_5H_5N (to absorb the liberated HBr) leads to *dibromogmelinol* (V), m.p. 145°, whilst (IV) in glacial AcOH is transformed by Br into *dibromoisogmelinol* (VI), m.p. 196°. A mixture of (V) and (VI) is obtained when (I) is brominated in AcOH. (V) is isomerised to (VI) when boiled with EtOH and conc. HCl. (V) and (VI) are unchanged by boiling aq. or alcoholic alkali or boiling C_5H_5N , showing that Br is probably a substituent on an aromatic nucleus. Both substances resist oxidation by $KMnO_4$. 4-Bromo-5-nitroveratrole is the sole isolable product of their oxidation with conc. HNO_3 , thus again emphasising the probability of the presence of two veratryl residues in (V) and (VI), each of which is substituted during bromination. The saturated nature of (I) is evidenced by the non-absorption of H_2 in presence of Pd-norit. It is reduced by Na and boiling EtOH or amyl alcohol to a pale yellow, viscous liquid which is not phenolic, indicating the absence of a coumarone or catechin type of mol. The available evidence suggests the structure $(C_3H_3O_2)(OH)[>CH \cdot C_6H_3(OMe)_2]_2$ for (I).

H. W.

Triterpenes. XLIV. Transformation of glycyrrhetic acid into β -amyrin. L. RUZICKA and A. MARXER (Helv. Chim. Acta, 1939, 22, 195—201).—Deoxyglycyrrhetic acid (A., 1937, II, 510) is transformed by Ac_2O in abs. C_5H_5N at 100° into *acetyldeoxyglycyrrhetic acid* (I), m.p. 309—310° after softening at 304°, [α_D^{20} +115.8° in $CHCl_3$, converted by $SOCl_2$ at 100° into *acetyldeoxyglycyrrhetyle chloride*, m.p. 248—251°, which is reduced (Pd- $BaSO_4$ in xylene at 155°) to *acetyldeoxyglycyrrhetaldehyde*, m.p. 243—246° after softening at 238° [oxime, m.p. 252—255° (decomp.)]. The corresponding *semicarbazone*, m.p. 342° when placed in bath at $\geq 230^\circ$ or m.p. $\sim 340^\circ$ after

re-solidification if placed in bath at a higher temp., is transformed by NaOEt-EtOH at 200° into β -amyrin, m.p. 190—102° after slight softening, $[\alpha]_D +90.0^\circ$ in CHCl_3 (Ac, m.p. 241—242°, $[\alpha]_D +81.2^\circ$ in CHCl_3 , and Bz, m.p. 232—234°, derivatives), and *hydroxy- β -amyrin*, $\text{C}_{30}\text{H}_{50}\text{O}_2$, m.p. 241—243°, $[\alpha]_D +87.2^\circ$ in CHCl_3 (*diacetate*, m.p. 198° after softening at 182°, $[\alpha]_D +96.19^\circ$ in CHCl_3), which greatly depresses the m.p. of erythrodil and soyasapogenol C. With CrO_3 in AcOH, (I) gives the modification of acetylglucyrrhetic acid, m.p. 322—325°, $[\alpha]_D +141.2^\circ$ in CHCl_3 , and an *acetylketolactone*, $\text{C}_{32}\text{H}_{48}\text{O}_{53}$, m.p. 319—322° after softening at 308°, $[\alpha]_D +134.5^\circ$ in CHCl_3 . All m.p. are corr. H. W.

Constituents of pyrethrum flowers. XIV. Structures of the enols of pyrethrolone. H. L. HALLER and F. B. LA FORGE (J. Org. Chem., 1939, 3, 543—549; cf. A., 1938, II, 372; Staudinger and Ruzicka, A., 1924, i, 522, 523).—Tetrahydropyrethrolone is converted by boiling KOH-EtOH containing Zn dust into some optically inactive tetrahydropyrethrolone and *tetrahydroisopyrethrolone enol* (I), b.p. 150°/0.25 mm., identical with the compound obtained by hydrogenating isopyrethrolone enol (II), b.p. 105—160°/0.7 mm. [*acetate* (III), b.p. 118—120°/4 mm.], obtained by Staudinger *et al.* (*loc. cit.*) together with pyrethrolone enol by the action of NaOMe on pyrethrolone. (I) is converted by Ac_2O at 100° into its *acetate* (IV), b.p. 115—120°/0.35 mm., which is rapidly hydrogenated (PtO_2 in EtOAc) to a product (V), b.p. 67—70°/2 mm.; this is transformed by $\text{NH}_2\text{-CO-NH-NH}_2\text{-HCl-C}_5\text{H}_5\text{-N-H}_2\text{O-EtOH}$ into two isomeric *semicarbazones*, m.p. 206° and 140—142° respectively. (II) gives an acetate which absorbs 4 H_2 giving two *isohexahydropyrethrones*, isolated as *semicarbazones* identical with those derived from (V). Partial hydrogenation of (III), involving only the double linkings in the side-chain, is effected by PtO_2 in denatured EtOAc, thus giving (IV). (II) is therefore regarded as *2-hydroxy-4-methyl-3-pentadienyl- Δ^2 -cyclopenten-1-one* and the *isohexahydropyrethrones* as *4-methyl-3-amyleycyclopentan-1-ones*. H. W.

Xanthoxylin S, a constituent of Xanthoxylum carolinianum. II. H. DIETERLE and K. SCHWENGLER (Arch. Pharm., 1939, 277, 33—44; cf. A., 1931, 1199).—Xanthoxylin S (I) contains two methylenedioxyresorcinol nuclei and probably has a formula of the type suggested by Erdtmann (A., 1937, II, 28, 69). (I), new formula, $\text{C}_{20}\text{H}_{18}\text{O}_6$, m.p. 121°, $[\alpha]_D^{25} -122^\circ$, with $\text{HNO}_3\text{-AcOH}$ gives 68% of a (NO_2)₂-derivative (II), m.p. 221°, and 60% of 1:2:4- $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:NO}_2$. With $\text{H}_2\text{-Pd-C}$ (I) absorbs 2 H_2 with ring fission to give a *diol* (2 active H; *dibenzoate; diacetate*). $\text{H}_2\text{-Pd-C}$ converts (II) into a *diamino-alcohol*, m.p. 129—132° (2 CH_2O_2), but Sn-HCl-AcOH gives *diaminoxanthoxylin S* and thence a *diol*, oxidised by H_2O_2 to an acid, $\text{C}_8\text{H}_{10}\text{O}_8$, m.p. 187°. *l*-Asarinin (Huang-Minlon, A., 1937, II, 298) is identical with (I). Myristic acid, vanillin, a coumarin (Me ether, m.p. 107°), and the sterol, $\text{C}_{27}\text{H}_{46}\text{O}$, m.p. 141°, were isolated from *X. carolinianum*. R. S. C.

m-Dinitrobenzene reaction of ouabain and its application to the examination of East African arrow poison. W. D. RAYMOND (Analyst, 1939,

64, 113—115).—The reaction (cf. A., 1938, II, 344) is not sp. to ouabain (I) but is also given by members of the digitoxin group. A colorimetric method of determination based on the reaction is described, and the % of (I) in some arrow poisons so determined was checked by determining the lethal dose when injected into frogs. The botanical source of the principles present in some arrow poisons is discussed.

E. C. S.

Secretin picrolonate, m.p. 234—235° (decomp.).—See A., 1939, III, 270.

Sulphite cooking process. II. Reaction between thioglycollic acid and spruce lignin. C. E. AHLM and F. E. BRAUNS (J. Amer. Chem. Soc., 1939, 61, 277—280; cf. B., 1938, 1025).—Spruce lignin and $\text{SH-CH}_2\text{-CO}_2\text{H}$ in 2N-HCl at 100° give the acid (I), $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_5(\text{OH})_5(\text{SH-CH}_2\text{-CO}_2\text{H})_4$, converted by CH_3N_2 into the *ether ester*, $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_6(\text{OH})_4(\text{SH-CH}_2\text{-CO}_2\text{Me})_4$ (*tetra-acetate*), which with $\text{Me}_2\text{SO-NaOH}$ is partly methylated to give the *ether*, $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_{10}(\text{SH-CH}_2\text{-CO}_2\text{Me})$ and is partly decomposed and hydrolysed to the acid, $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_6(\text{OH})_4(\text{SH-CH}_2\text{-CO}_2\text{H})_2$. PhOH replaces 2 $\text{SH-CH}_2\text{-CO}_2\text{H}$ of (I). At most one $\text{SH-CH}_2\text{-CO}_2\text{H}$ of (I) is linked to a phenolic group.

R. S. C.

Lignin. XX. Union of formaldehyde in lignin. K. FREUDENBERG, F. KLINCK, E. FLICKINGER, and A. SOBEK (Ber., 1939, 72, [B], 217—226).—Distillation with mineral acids cannot lead to a decision with respect to the mode of formation of CH_2O from lignin (I). A more suitable reagent is NH_2Ph containing some HCl which gives (readily isolated) acridane (II) with aromatic CH_2O_2 -compounds and polyoxymethylenes but not with $\text{CHPh:CH-CH}_2\text{-OH}$ and its ether, coniferin, or fructose. Intact (I) and pine wood afford (II), which is not obtained from Tornesch lignin. The presence of CH_2O_2 groups in (I) is established by the formation of CH_2O under the action of acids and of NH_2Ph and by the observation that the ratio between the amounts of CH_2O found by the two processes is the same for (I) as for piperonylic acid (III). CH_2O is not obtained from 28% H_2SO_4 and $\text{CH}_3\text{Ph-OH}$, $(\text{CH}_2\text{Ph})_2\text{O}$, $\text{CH}_2\text{Ph-CH}_2\text{-OH}$, CHPh:CH-CHO , geraniol, $\text{CH}_2\text{Bz-OH}$ (IV) and its $(\text{OMe})_2$ -derivative, and veratroylcarbinol. (IV) yields PhCHO but CH_2O could not be detected. Phenylglycol gives PhCHO and an unidentified compound, m.p. 161°. CH_2O can no longer be detected in (I) which has been reprecipitated from a solution of K in liquid NH_3 . Under these conditions (III) is transformed into *m*- $\text{OH-C}_6\text{H}_4\text{-CO}_2\text{H}$ and dihydrosafrole into *p*- $\text{C}_6\text{H}_4\text{Pr-OH}$. It is therefore beyond doubt that CH_2O in lignin is present entirely or predominantly in aromatic CH_2O_2 groups. The relationships of pine and beech (I) are discussed. Unsuccessful attempts are described to isolate from (I) fragments containing CH_2O_2 . It is concluded that there are no such terminal groups but that the aromatic CH_2O_2 complexes are built into the interior of the mol. of (I).

H. W.

Sulphuric esters of the components of pine wood. K. FREUDENBERG and R. KELLER (Ber., 1939, 72, [B], 331—334).—Pine wood is transformed

by $C_5H_5N-H_2SO_4$ into a pale-coloured product, the amount and composition of which suggest that each polysaccharide unit has combined with three and each lignin (I) unit with one $SO_3 \cdot C_5H_5N$ group. It is divided by hot and cold H_2O into several fractions and further purification is effected by taking advantage of the insolubility of the K salts of polysaccharide ester in an excess of KOH. Portions containing (I) are to some extent sol. in excess of alkali and are salted out when the solution is neutralised. Thus are obtained (a) salts of polysaccharide sulphuric esters (II) free from OMe, (b) salts of lignin sulphuric esters free from sugar and corresponding with a sulphuric ester salt derived from cuproxam lignin, and (c) mixtures of (II) with salts of sulphuric esters derived from compounds of carbohydrates and (I). In (b) and (c) all the OMe of the wood is found. H. W.

Lignin and related compounds. XXXV. Ethanolysis of spruce wood. A. B. CRAMER, M. J. HUNTER, and H. HIBBERT. **XXXVI.** Ethanolysis of maple wood. M. J. HUNTER, A. B. CRAMER, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 509—516, 516—520; cf. A., 1938, II, 238).—XXXV. The extract obtained from spruce wood-meal by 1:1 EtOH- C_6H_6 is heated with 3% HCl-abs. EtOH. The phenols, b.p. 130—150°/0.01 mm., of the H_2O -sol. portion of the product give, when treated with CH_2N_2 , 4- α -ethoxypropioveratrone (I), m.p. 81—82° (2:4-dinitrophenylhydrazone, m.p. 140—141°), stable to NaOH, oxidised by $KMnO_4$ -NaOH to 3:4-(OMe) $_2$ C_6H_3 -CO $_2$ H. OEt-[CH $_2$] $_2$ -CN (prep. from the bromide and KCN), b.p. 75—77°/23 mm., with HCl gives OEt-[CH $_2$] $_2$ -CO $_2$ H, b.p. 121°/20 mm., the chloride, b.p. 64—67°/30 mm., of which with $AlCl_3$ and veratrone (II) in CS_2 at $\geq 20^\circ$ gives 4- β -ethoxypropioveratrone, m.p. 50—51° (2:4-dinitrophenylhydrazone, m.p. 167—168°), better obtained from 3:4-(OMe) $_2$ C_6H_3 -CO-[CH $_2$] $_2$ -Cl, NaI, and EtOH. OMe-CHMe-COCl (II), and $AlCl_3$ in CS_2 give a compound [not (I)], $C_9H_7O(OMe)_2$ -OEt, m.p. 81—82°. Propioveratrone and Br-CHCl $_3$ give the α -Br-derivative, m.p. 89°, which with KOAc in abs. EtOH gives the α -OAc-compound, m.p. 65—66°, converted by 2% HCl-abs. EtOH into (I) or by $BaCO_3$ in hot H_2O into 4- α -hydroxypropioveratrone (III), b.p. 140°/0.01 mm. 1% HCl-abs. EtOH decomposes (III) at 0°, but hot 0.5% HCl-abs. EtOH converts it into (I). It is probable that 4- α -hydroxypropiovanillone, its dienol, 4:3-OH- $C_6H_3(OMe)_2$ -CHAc-OH, or some precursor readily transformed into one of these isomerides occurs in spruce lignin as precursor of the various substances obtained therefrom.

XXXVI. Maple wood yields, by similar methods, phenols, which with CH_2N_2 give (I) and with p -NO $_2$ - C_6H_4 -COCl- C_5H_5N give 5- α -ethoxypropiosyringone p -nitrobenzoate (IV), m.p. 140—142°. 3:4:5-(OMe) $_3$ C_6H_2 -COEt (improved prep.) and Br give α -bromo-3:4:5-trimethoxypropiofenone, m.p. 83—84°, converted by H_2SO_4 at 45—47° into 5- α -bromopropiosyringone, m.p. 89—90°, and thence by NaOAc-AcOH (not KOAc-EtOH) into the α -OAc-compound, m.p. 172—173°, which with 2% HCl-abs. EtOH yields 5- α -hydroxypropiosyringone, b.p. 160—180°/0.007 mm. [gives (IV)]. Pyrogallol 1:3-Me $_2$ ether 2-propionate,

b.p. 125—127°/0.5 mm., and $AlCl_3$ in $PhNO_2$ give propiosyringone, m.p. 109—110°, also obtained from 3:4:5-(OMe) $_3$ C_6H_2 -COEt and conc. H_2SO_4 . The presence of α -hydroxypropio-veratrone and -syringone in maple lignin is thus indicated. R. S. C.

Aldehydic constituents from the ethanolysis of spruce and maple woods. L. BRICKMAN, J. J. PYLE, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 523).—The products obtained from spruce and maple woods by HCl-EtOH include an aldehyde, $C_{11}H_{12-14}O_5$ (semicarbazone, m.p. 210—210.5°), probably α - or β -keto- β -4-hydroxy-3:5-dimethoxyprop-aldehyde. R. S. C.

Reconversion of an "extracted" lignin into its primary building units. Q. P. PENISTON, J. L. MCCARTHY, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 530).—Acetylated oak lignin (OMe 8.7, Ac 35%) and hot 2% HCl-EtOH give a mixture closely resembling that obtained directly by HCl-EtOH from maple wood. R. S. C.

Pantothenic acid. III. Analysis and determination of constituent groups. R. J. WILLIAMS, H. H. WEINSTOCK, jun., E. ROHRMANN, J. H. TRUESDAIL, H. K. MITCHELL, and C. E. MEYER (J. Amer. Chem. Soc., 1939, 61, 454—457; cf. A., 1939, III, 100).—Quant. oxidation, analysis, and loss, retention, or recovery of biological activity under the influence of reagents show pantothenic acid to be $C_8H_{15}O_5N$, containing CO $_2$ H, 2 OH, and (?) $\cdot CO \cdot NH \cdot$, but not other simple groups. It is not an α -OH-acid and contains no aromatic ring (absorption spectrum). R. S. C.

Composition of the so-called pyroabietic acid prepared without a catalyst. E. E. FLECK and S. PALKIN (J. Amer. Chem. Soc., 1939, 61, 247—249).—Pyroabietic, prepared by heating at 340° *l*-abietic acid, $[\alpha]_D^{20} -104^\circ$ in EtOH, contains dehydroabietic acid, m.p. 172—173°, $[\alpha]_D^{20} +62^\circ$ in EtOH, and the H_2 -lactone, m.p. 130—131°, $[\alpha]_D^{20} -4^\circ$ in EtOH, but not the H_4 - or H_2 -acid, $[\alpha]_D^{20} +108^\circ$. The lactone gives the hydroxytetrahydro-acid, m.p. 164—165°, $[\alpha]_D^{20} +35^\circ$ in EtOH. R. S. C.

α -Di-iodobutane from tetrahydrofuran. G. B. HEISIG (J. Amer. Chem. Soc., 1939, 61, 525—526).—Tetrahydrofuran (prep. in 91% yield from furan by H_2 -Raney Ni at 80°) and red P-I give 51% of ($\cdot CH_2 \cdot CH_2 I$) $_2$, b.p. 105—110°. R. S. C.

3-Chloro-2-alkoxy-2-methyltetrahydrofurans.—See B., 1939, 245.

Orientation in the furan series. XI. Cleavage-rearrangements in Friedel-Crafts reactions. H. GILMAN and J. A. V. TURCK, jun. (J. Amer. Chem. Soc., 1939, 61, 473—478; cf. A., 1938, II, 866).—Et 5-bromo-4-*tert*-butyl-2-furoate (I) is obtained as sole cyclic product from Et 5-bromo-2-furoate, $AlCl_3$, and Bu n Cl, Bu n Br, n - $C_5H_{11}Cl$, *iso*- $C_5H_{11}Br$, CM_2EtCl , n - $C_5H_{11}I$, n - $C_6H_{13}Cl$, n - $C_6H_{13}Br$, n - $C_{12}H_{25}Br$, n - $C_8H_{17}Br$, or n - $C_{18}H_{37}Br$ (46% yield) in CS_2 . $CM_2Et \cdot OH$ leads to 5-bromo-4-*tert*-butylfuroic acid, but $CH_3Et \cdot CH_2$, diisobutylene, n - Δ^3 -pentene, and cyclohexene do not react. n - $C_5H_{11}Br$ gives (I) or Et 5-*tert*-butyl-2-furoate (II) or mixtures of the two according to the conditions, but Et 5-chloro-2-furoate

gives only the 4-Bu^v derivative (hydrolysed by KOH to 5-chloro-4-tert.-butyl-2-furoic acid, m.p. 172—173°). Et 4-bromo-2-furoate and *n*-C₅H₁₁Cl give only (II), the Br being lost after condensation. No reaction occurs with Et 4 : 5-dibromo-2-furoate and *n*-C₅H₁₁Br or 5-bromofurfuraldehyde and *n*-C₅H₁₁Cl. FeCl₃ alone does not induce alkylation of furates, but presence of traces thereof in AlCl₃ slightly increases the yields and increases the amount of (II) formed at the expense of the (I). <1 mol. of AlCl₃ is required for reaction of alkyl halides, probably owing to complex formation with the CO₂Et. The reaction mechanism is discussed. When *n*-C₅H₁₁Cl is used, *n*- and *iso*-C₄H₁₀ are formed with smaller amounts of products of lower mol. wt.; if no solvent is used, C₄H₁₀, C₅H₁₂, and resins are formed. With *n*-C₁₈H₃₇Br in (CHCl₂)₂, C₄H₁₀, C₅H₁₂, C₆H₁₄, and higher products are obtained. Details of the effect of concn. and reaction time are given. Et 5-bromo-2-furoate, *tert*-C₅H₁₁Ph, and AlCl₃ give small amounts of an acid, C₁₁H₁₆O₂, m.p. 187—187.5°. R. S. C.

Raney nickel applied to the hydrogenation of furanocarboxylic acids. R. PAUL and G. HILLY (Compt. rend., 1939, 208, 359—361; cf. A., 1937, II, 298; 1938, II, 346).—Pyromucic acid, furylacrylic acid (I), and furfurylidenemalononic acid dissolved in the theoretical quantity of NaOH with H₂—Raney Ni at 100—110° under pressure afford tetrahydrofuran-2-carboxylic acid, b.p. 128—129°/13 mm., and -furylpropionic acid, b.p. 156—157°/15 mm. Pyromucamide in EtOAc similarly affords tetrahydrofuran-2-carboxylamide, m.p. 78—79°. Et pyromucate, furylacrylate, furfurylidene-malonate and -acetoacetate with Raney Ni—H₂ at 100—110° under pressure afford Et tetrahydrofuran-2-carboxylate, b.p. 80°/11 mm., β-tetrahydrofurylpropionate, b.p. 110°/15 mm., tetrahydrofurfurylmalonate, b.p. 166—167°/17 mm., and β-hydroxy-α-tetrahydrofurfurylbutyrate, b.p. 152—153°/10 mm., respectively. (I) gives some γ-propylbutyrolactone when reduced. J. L. D.

Side-chain derivatives of pyromucic acid. E. VOROČEK and A. KROŠLÁK (Coll. Czech. Chem. Comm., 1939, 11, 47—53).—2-Aldehydofuran-5-carboxylic acid (I) (*Me* ester phenylhydrazone, m.p. 183°) when heated with CH₂(CO₂H)₂ in C₅H₅N, and the product hydrolysed (dil. H₂SO₄), yields β-(2-carboxyfuryl)-acrylic acid (II), m.p. 273—274° [*Me* ester {from the *Me* ester of (I)}, m.p. 206—208°], together with a compound, m.p. >300°. Distillation of (II) gives a substance, m.p. 132—134°, containing C 56.6, H 4.7%. (II) is reduced (Na—Hg) to the -5-propionic acid, m.p. 180°. The *Me* ester of (I), when treated with N₂H₄·H₂O in Et₂O, and the product heated with EtOH—NaOEt at 150—160°, yields 2-methylfuran-5-carboxylic acid, when boiled with H₂O—EtOH—KCN yields 2-carbomethoxyfuran-5-glycollic acid, m.p. 238—239°, and with CH₃N₂ yields *Me* 5-acetylfuran-2-carboxylate, m.p. 103°. A. Lr.

Properties of some isomeric 1 : 4- and 1 : 5-epoxides. R. PAUL (Bull. Soc. chim., 1939, [v], 6, 331—335; cf. A., 1938, II, 289).—Physical consts., e.g., b.p., *n*, *η*, mol. vol., and parachor, of isomeric 2-alkyltetrahydro-furans (I) and -pyrans (II) are compared. Although generally, b.p. of (I) are 6—7°

> those of (II), an exception is the case of 2-benzyl-tetrahydrofuran, b.p. 109—110°/10 mm., compared with 2-phenyltetrahydropyran, b.p. 111—112°/10 mm.

A. T. P.

Synthesis of bis-(5-hydroxymethylfurfuryl-acrylic acid) ether. K. Aso (J. Agric. Chem. Soc. Japan, 1939, 15, 56).—The substance, m.p. 203—204° (decomp.), is obtained from ω-hydroxymethylfurfuraldehyde ether by Perkin's reaction. J. N. A.

Decomposition products of substances containing uronic acid by heating in autoclave. II. Reduction of dimethylalginetin. K. Aso (J. Agric. Chem. Soc. Japan, 1939, 15, 57—58; cf. A., 1935, 753).—Dimethyltetrahydroalginetin [4-hydroxy-3 : 8-dimethoxy-2-methylchroman], m.p. 182° (acetate, m.p. 117°), is formed by catalytic reduction of dimethylalginetin [3 : 8-dimethoxy-2-methylchroman]. J. N. A.

6-Hydroxy-2 : 5 : 7 : 8-tetramethyl-2-80-dimethylnonylchroman (allophanate, m.p. 170°).—See A., 1939, III, 169.

Synthesis of 6-hydroxy-8-methoxycoumarin. F. MAUTHNER (J. pr. Chem., 1939, [ii], 152, 23—26).—8-Methoxycoumarin [prep. from *o*-vanillin (I), anhyd. NaOAc, and Ac₂O at 170—175° described] is oxidised by K₂S₂O₈ in alkaline solution containing FeSO₄ at 16—18° to 6-hydroxy-8-methoxycoumarin, m.p. 239—240°. Hippuric acid, anhyd. NaOAc, Ac₂O, and (I) at 115—120° afford α-3-methoxy-2-acetoxybenzimidocinnamic anhydride, m.p. 158—159°, and 3-benzamido-8-methoxycoumarin, m.p. 207—208°. H. W.

Heterocyclic compounds. IX. Coumarins from substituted resacetophenones and acetoacetic ester. R. D. DESAI and M. EKHLAS (Proc. Indian Acad. Sci., 1938, 8, A, 567—577; cf. A., 1938, II, 152, 373).—CH₂Ac·CO₂Et, 2 : 4-(OH)₂C₆H₃·COMe, and POCl₃·C₆H₆ at 100° (bath) (general method A) give 7- (I), m.p. 212° (carbethoxy-derivative, m.p. 141°) and a little 5-hydroxy-6-acetyl-4-methylcoumarin, m.p. 164—165°. (I) is reduced (Clemmensen) to 7-hydroxy-4-methyl-6-ethylcoumarin. 2 : 4-Dihydroxy-5-ethylacetophenone gives (method A) 5-hydroxy-6-acetyl-4-methyl-8-ethylcoumarin (II), m.p. 169° (*Me* ether, m.p. 173°; *Ac* derivative, m.p. 149°; semicarbazone, m.p. >285°), reduced by Zn—Hg to 5-hydroxy-4-methyl-6 : 8-diethylcoumarin. (II) and Ac₂O—NaOAc at 170—180° (oil-bath) give 5-acetyl-4' : 6-dimethyl-8'-ethylcoumarino-5' : 6'-2 : 3-γ-pyrone, m.p. 173°. *Me* 2 : 4-dihydroxy-5-ethylbenzoate, CH₂Ac·CO₂Et, and 73% H₂SO₄ at 0° afford *Me* 5-hydroxy-4-methyl-8-ethylcoumarin-6-carboxylate, m.p. 185—186°, converted by 10% aq. NaOH at room temp. (3 days) into the 6-carboxylic acid, m.p. 240° (decomp.), decarboxylated at 250° to 5-hydroxy-4-methyl-6-ethylcoumarin, m.p. 211—212°, the *Ac* derivative, m.p. 112—113°, of which is transformed (Fries) by AlCl₃ at 140—145° (oil-bath) into (II). 2 : 4-Dihydroxy-6-methylacetophenone [A] affords 5-hydroxy-6-acetyl-4 : 7-dimethylcoumarin (III), m.p. 178° (*Ac* derivative, m.p. 160°; semicarbazone, m.p. >280°), and some 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258—259° [*Ac* derivative, m.p. 202°, is transformed into (III) (Fries)], also obtained from orcinol and CH₂Ac·CO₂Et. Gallacetophenone [A] gives 7 : 8-

dihydroxy-6-acetyl-4-methylcoumarin, m.p. 148° [not obtained from 7:8-diacetoxy-4-methylcoumarin (Fries)], and 2:4-dihydroxypropionophenone [A] affords 7-hydroxy-6-propionyl-4-methylcoumarin, m.p. 227—228° (cf. Limaye *et al.*, Rasáyanam, 1937, 1, 96) (Ac derivative, m.p. 132°; semicarbazone, m.p. >285°; carbethoxy-derivative, m.p. 132°; 3-Br-derivative, m.p. 140°), converted by $\text{Ac}_2\text{O}-\text{NaOAc}$ at 170—180° into 4:2':3'-trimethylcoumarino-7:6- γ -pyrone, m.p. >270°. 7-Hydroxy-6-butyryl-4-methylcoumarin, m.p. 151° (Ac derivative, m.p. 156°), is converted into 4:2'-dimethyl-3'-ethylcoumarino-7:6- γ -pyrone, m.p. 244—245°. $m\text{-C}_6\text{H}_4(\text{OH})_2$ and $\text{BzCl}-\text{AlCl}_3-\text{PhNO}_2$ at room temp. (48 hr.) give 4-benzoylresorcinol, m.p. 145°, in 70% yield (cf. A., 1936, 1245), which [A] affords 7-hydroxy-6-benzoyl-4-methylcoumarin, m.p. 180° (semicarbazone, m.p. 240°), converted into 4-methyl-4'-phenylcoumarino-7:6- α -pyrone, m.p. 255°. Resacetophenone and Br-AcOH at room temp. (24 hr.) give the 5- or 3-Br-derivative (V), m.p. 167° (Me_2 ether, m.p. 146°; Ac_2 derivative, m.p. 161—162°), and a little Br_2 -compound, m.p. 173—174°. (V), β -Me resacetophenone-carboxylate, 2:4- or 4:6-diacetylresorcinol, and quinacetophenone (indefinite) do not react [A]. 4-Acetyl-, -propionyl, or -butyryl- α -naphthol with $\text{CH}_2\text{Ac}-\text{CO}_2\text{Et}$ and H_2SO_4 or POCl_3 gives only 4-methyl-1:2- α -naphthapyrone. Thus substituents as Br, CO_2Me , and acyl hinder the coumarin condensation, this effect in the case of COR groups being in the order $\text{R} = \text{Ph} > \text{Me} > \text{Et} > \text{Pr}$. An electronic conception of the effect of substituents is discussed.

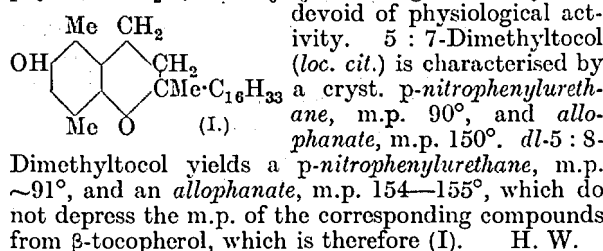
A. T. P.

Esters of α -tocopherol. V. DEMOLE, O. ISLER, B. H. RINGLER, H. SALOMON, and P. KARRER (Helv. Chim. Acta, 1939, 22, 65—68).—*dl*- α -Tocopheryl acetate (I), b.p. 184°/0.01 mm., is obtained from *dl*- α -tocopherol (II), anhyd. $\text{C}_6\text{H}_5\text{N}$, and Ac_2O at room temp. and then at 60° or by condensing trimethylquinol with phytol bromide by ZnCl_2 in light petroleum and treating the product with Ac_2O containing H_2SO_4 at 40°. (I) is not autoxidisable and is not attacked by AgNO_3 or AuCl_3 . The corresponding *propionate* and *butyrate*, b.p. 230°/0.25 mm., are described. The *hexoate*, *succinate*, *benzoate*, and *stearate* have been prepared; the last of these is cryst. The esters are not inferior to (II) in vitamin-E activity. H. W.

Potentiometric determination of the tocopherols. Behaviour of *dl*- α -tocopherol when irradiated. P. KARRER and H. KELLER (Helv. Chim. Acta, 1939, 22, 253—259).—The following method is recommended for the elimination of the "carotenoid" error in the potentiometric determination of tocopherols (I) by titration with AuCl_3 (A., 1938, II, 450). The total reducing matter is determined in one sample of the unsaponifiable matter. A second sample is fully acetylated by treatment with Ac_2O in $\text{C}_6\text{H}_5\text{N}$ at 100° for 2 hr. The mixture is diluted with light petroleum and the solution is washed with dil. HCl and then with H_2O until neutral. After removal of the light petroleum the residue is determined potentiometrically. Since (I) are thereby converted into their non-reducing acetates, the reducing power of the acetylated sample is ascribed entirely

to the carotenoids. The difference between the two titrations is \propto (I). Solutions of *dl*- α -tocopherol in EtOH gradually lose their reducing power when exposed to ultra-violet light in presence or absence of air; the product has not been identified. H. W.

Lower homologues of α -tocopherol. β -Tocopherol. Constitution-specificity of vitamin-E action. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1939, 22, 260—263; cf. A., 1938, II, 450).—For the production of max. vitamin-E activity the presence of 3 Me groups in the aromatic nucleus of tocol is necessary (α -tocopherol). Substances with 2 Me in any positions are active but the therapeutic dose is 3—4 times that of the Me_3 compound. A single Me in the aromatic nucleus is not causative of -E activity. Since it does not appear possible to replace the phytol residue by another group without loss of -E activity, the conditions necessary for an active product appear very narrow. $m\text{-OH}-\text{C}_6\text{H}_4\text{-OMe}$, phytol, HCO_2H , and C_6H_5 at 100° give a *methyltol*, devoid of physiological activity. 5:7-Dimethyltol (loc. cit.) is characterised by a cryst. *p*-nitrophenylurethane, m.p. 90°, and *allophanate*, m.p. 150°. *dl*-5:8-Dimethyltol yields a *p*-nitrophenylurethane, m.p. ~91°, and an *allophanate*, m.p. 154—155°, which do not depress the m.p. of the corresponding compounds from β -tocopherol, which is therefore (I). H. W.



Constitution of the compound obtained from trimethylquinol and crotyl bromide. P. KARRER and R. ESCHER (Helv. Chim. Acta, 1939, 22, 264).—The formation of COMe_2 when the compound is oxidised (Oppenauer) and then degraded with CrO_3 shows that it is 6-hydroxy-2:5:7:8-tetramethylchroman as previously assumed (A., 1938, II, 450). H. W.

Specificity of vitamin-E action. F. VON WERDER, T. MOLL, and F. JUNG (Z. physiol. Chem., 1939, 257, 129—139; cf. A., 1938, II, 359; 1939, II, 82).—The following were active in the doses mentioned: 3 mg., *dl*- α -tocopherol; 50 mg., 6-acetoxy-2:5:7:8-tetramethylchromone; 100 mg., 2:5-dimethylquinol, duroquinol (I) and its *n*-nonadecyl ether, m.p. 105—106° [from the mother-liquors from (II)], ψ -cymoquinol (IV) and its *benzoate*, m.p. 150—151° [from trimethylquinol (III) in $\text{C}_6\text{H}_5\text{N}$ in a stream of H_2 and BzCl], and chroman. The following were inactive in the doses given: 20 mg., α -tocopherylquinone; 30 mg., 2:5:7:8-tetramethylchroman, m.p. 48° [obtained by reduction ($\text{Pt}-\text{H}_2$) of the corresponding chromone in 96% AcOH], and 5-hydroxy-2:4:6:7-tetramethylcoumarone; 50 mg., the ϵ -(1':1':3'-trimethyl-2'-cyclohexyl)- γ -methylamyl ether (*allophanate*, m.p. 173—174°) of (I) [from (I)] and ϵ -(1':1':3'-trimethyl-2'-cyclohexyl)- γ -methylamyl bromide (V) in EtOH at 80° in a stream of H_2 with KOH in EtOH, the product being adsorbed on Al_2O_3 and eluted with light petroleum, 1:2:4:5:3:6- $\text{C}_6\text{Me}_3\text{Ac}(\text{OH})_2$ and $\text{-C}_6\text{Me}_3\text{Et}(\text{OH})_2$; 100 mg., 2:6-dimethylquinol, the *bis*-*n*-nonadecyl ether (II), m.p. 97—98° of (I) [from (I) and *n*-nonadecyl bromide in EtOH in a stream of H_2 at 85° with KOH in EtOH], the *bis*- β -iodopropionate,

m.p. 126—127°, of (IV) [from (III) and $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{COCl}$ in PhNO_2 under N_2 with AlCl_3], 2 : 3-dimethylnaphthoquinone, coumaran, 6-hydroxy-2 : 5 : 7 : 8-tetramethylchroman, m.p. 145° (from the corresponding chromone in 96% AcOH and Pt-H_2), 5-hydroxy-2 : 4 : 6 : 7-tetramethylcoumaran, and 6-deoxy-dl- α -tocopherol, b.p. 180—182°/0.1 mm. [from 1 : 2 : 3 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$ in light petroleum with $o\text{-C}_6\text{H}_4(\text{COBr})_2$ and ZnCl_2 , impurities being removed from the product by adsorption on Al_2O_3]. The high toxicity of naphthoquinone in doses of 50 and 100 mg. prevents its activity from being determined with rats. The prep. of the following is described: the 4- β -methylamyl ether (allophanate, m.p. 206°) of (I) [from (I) and $\text{CHMeBu}^{\beta}\text{Br}$ in EtOH in a current of H_2 at 85° and n-KOH in EtOH], $\text{n-nonadecyl bromide}$, m.p. 38—39° [from the Et ester of the corresponding acid by reduction (EtOH-Na) and treatment of the resulting $\text{n-nonadecyl alcohol}$ with PBr_3], an allyl ether, m.p. 83—84° (probably 2 : 3 : 6-trimethyl-1-allylquinol), of (III) [from (IV) at 60° in N_2 and $\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Br}$ with KOH in EtOH followed by adsorption of the product on Al_2O_3 and elution with C_6H_6 -light petroleum], the n-octyl , m.p. 72—73° [from (IV) and $\text{C}_8\text{H}_{17}\text{I}$ in EtOH at 80° in H_2 with n-KOH in EtOH followed by distillation of the product and crystallisation and adsorption on Al_2O_3 of the portion of b.p. 180—185°/1.5 mm.], and the ϵ -(1' : 1' : 3'-trimethyl-2'-cyclohexyl)- γ -methylamyl ether (allophanate, m.p. 128°) of (IV) [from (III) and (V) in EtOH with KOH in EtOH at 85° followed by distillation of the product, the fraction of b.p. 200°/0.8 mm. being converted into allophanate] and 2 : 5 : 7 : 8-tetramethyl- (VI), m.p. 116° (from 1 : 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{OH}$ in EtOAc and P_2O_5), and 5 : 7 : 8-trimethyl-2-styryl-chromone, m.p. 152° [from (VI), NaOH in EtOH , and PhCHO]. The absorption max. of the coumarans are at slightly longer λ than are those of the chromans. Possibly the simple chromans are inactive because of their stability which prevents them playing a part in a species of oxidation-reduction mechanism (quinol-quinone transformation). W. McC.

Antisterility factors (vitamin-E). VI. Oxidation products of tocopherols and of simple analogous models. W. JOHN, E. DIETZEL, and W. EMTE (Z. physiol. Chem., 1939, 257, 173—189; cf. A., 1938, II, 241, 359).—Details of the prep. of α -tocopherylquinone (I) are given; when AgNO_3 is the oxidising agent red substances are produced as a result of further oxidation. Such substances are also produced in greater yield during the prep. of β -tocopherylquinone (II) from β -tocopherol by oxidation with AgNO_3 ; this oxidation is also achieved with FeCl_3 . (I) in light petroleum is reduced to α -tocopherylquinol (III) (absorption curve almost identical with that of duroquinol) [triacetate, m.p. 75°, obtained by boiling (I) with Ac_2O , NaOAc , and Zn] by Pd-H_2 and by Zn-AcOH . (III) is very readily re-oxidised to (I) by atm. O_2 . α -Tocopherol (IV) is obtained from (I) by boiling in AcOH with Zn and HBr or by heating with Zn and HCl in EtOH and from (III) by heating with strong acid. Reductive esterification of (I) in Et_2O with $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COCl}$ and $\text{Na}_2\text{S}_2\text{O}_4$ gives a $\text{di-p-bromobenzoate}$, m.p. 114°, and treatment in

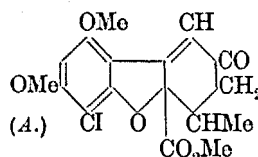
MeOH with Me_2SO_4 , NaOH , and $\text{Na}_2\text{S}_2\text{O}_4$ gives the Me_2 ether (dinitrobenzoate, m.p. 57°) of (III). Similarly (II) gives the Me_2 ether of β -tocopherylquinol. 6-Hydroxy-2 : 5 : 7 : 8-tetramethylchroman (V) (acetate, m.p. 102°; 6-OH not esterified) in EtOH oxidised with AgNO_3 gives red substances and a quinone (VI), m.p. 79° ($\text{di-p-bromobenzoate}$, m.p. 199°, of the corresponding quinol; OH of the side-chain not esterified, readily attacked by CrO_3 in AcOH), further oxidised by AgNO_3 to a red substance, $\text{C}_{12}\text{H}_{14}\text{O}_3$, m.p. 141° (absorption max. 275 and 365 $\text{m}\mu$) (cf. Karrer *et al.*, *ibid.*, 450), reconverted into (V) by Zn-AcOH . (VI), which is also obtained without production of red substances by oxidation of (V) with FeCl_3 , yields the triacetate, m.p. 104°, of 2 : 4 : 5-trimethyl-1- γ -hydroxybutylquinol when boiled with Ac_2O , NaOAc , and Zn . 6-Hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman (VII) in EtOH oxidised with FeCl_3 gives a quinone (VIII), m.p. 62° ($\text{di-p-bromobenzoate}$, m.p. 202°, of the corresponding quinol, resistant to oxidation by CrO_3), also obtained together with red substances when AgNO_3 replaces FeCl_3 . (VIII), which is further oxidised by AgNO_3 to a red substance, m.p. 109°, is reduced by Zn-AcOH to the corresponding quinol, little or no (VII) being produced, and is converted into the triacetate, m.p. 113°, of 2 : 4 : 5-trimethyl-1- γ -hydroxyisomylquinol by Ac_2O , NaOAc , and Zn . 6-Hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydrocoumarin is quantitatively oxidised by AgNO_3 to $\text{Et } \beta$ -2 : 4 : 5-trimethylbenzoquinonylpropionate, m.p. 59-6°, when the solvent is boiling EtOH and to the corresponding Me ester, m.p. 33°, when it is boiling MeOH . (I) has no vitamin-E activity. The monocetyl ether of duroquinol (IX) in COMe_2 boiled for 2 hr. with AgNO_3 is converted quantitatively into (IX) and cetyl alcohol. Other mono-ethers of (IX) and of ψ -cumoquinol are also hydrolysed in the same way by AgNO_3 and by FeCl_3 (cf. Karrer *et al.*, *ibid.*, 197). The light absorption max. of coumarans are higher and at shorter λ than are those of similarly substituted chromans. In (IV) the O bridge is probably united to *tert. C*. The tocopherols are probably chroman derivatives. W. McC.

Synthesis of 3 : 8-dimethoxyflavone. K. Aso (J. Agric. Chem. Soc. Japan, 1939, 15, 59—60).—The substance, m.p. 156—157°, is obtained by condensation of 2-hydroxy-3 : ω -dimethoxyacetophenone with Bz_2O and NaOBz . The absorption spectrum has max. at 332 and 392 $\text{m}\mu$. J. N. A.

Simultaneous multiple alkylation of phenols. Synthesis of a phenolic coumarone involving the condensation of diethyl ketone with resorcinol. J. B. NIEDERL and V. NIEDERL (J. Amer. Chem. Soc., 1939, 61, 348—350).— $m\text{-C}_6\text{H}_4(\text{OH})_2$ (1 mol.), COEt_2 (2 mols.), and HCl in AcOH at room temp. give 5-hydroxy-1-methyl-2-ethyl-4- α -ethylpropenyl-1 : 2-dihydrobenzofuran, m.p. 134—135° [acetate, m.p. 42°, b.p. 158°/4 mm. (dibromide, m.p. 168—170°); phenylurethane, m.p. 155—156°; Br-derivative dibromide, m.p. 165°]. R. S. C.

Biochemistry of micro-organisms. LX. Griseofulvin, a metabolic product of *Penicillium griseofulvum*, Dierckx. A. E. OXFORD, H. RAISTRICK, and P. SIMONART (Biochem. J., 1939, 33,

240—248; cf. A., 1935, 786).—The dry micro-organism, propagated at 30° for 65—85 days on a medium containing glucose, NaNO_3 , KH_2PO_4 , KCl , MgSO_4 , and FeSO_4 , yields ~1.5% of *griseofulvin* (I), probably



(4), m.p. 218—219°, $[\alpha]_{\text{D}}^{25} +417^\circ$ in COMe_2 (*oxime*, m.p. 226—227°; sinters 120°, melts with loss of gas 120—140°, resolidifies at $>140^\circ$). (I) in EtOH , hydrolysed with boiling $2\text{N-H}_2\text{SO}_4$, gives the corresponding free monocarboxylic acid, *griseofulvic acid* (II), $\text{C}_{16}\text{H}_{15}\text{O}_6\text{Cl}$, m.p. 256—260°, $[\alpha]_{\text{D}}^{25} +508^\circ$ as Na salt in aq. COMe_2 , further hydrolysed by boiling 0.5N-NaOH to *decarboxyfulvic acid* (III), $\text{C}_{15}\text{H}_{14}\text{O}_5\text{Cl}$, m.p. 138—140°, $[\alpha]_{\text{D}}^{25} -31^\circ$ in COMe_2 , and *norgiseofulvic acid* (IV), $\text{C}_{15}\text{H}_{13}\text{O}_6\text{Cl}$, m.p. 260° (decomp.), $[\alpha]_{\text{D}}^{25} +609^\circ$ as Na salt in H_2O . (III) and (IV) are also obtained directly from (I) by boiling with dil. aq. NaOH. (II) and (IV) in Et_2O with CH_2N_2 give (I) together with *isogriseofulvin*, $\text{C}_{17}\text{H}_{17}\text{O}_6\text{Cl}$, m.p. 198—200°, $[\alpha]_{\text{D}}^{25} +265^\circ$ in COMe_2 . Catalytic reduction (Pd - norit-H_2) of (I) in EtOAc gives *dihydrogriseofulvin*, m.p. 194—196°, $[\alpha]_{\text{D}}^{25} -33^\circ$ in COMe_2 (compound, m.p. 264—266°, probably 2:4-dinitrophenylhydrazone, with Brady's reagent), and *tetrahydrogriseofulvin*, $\text{C}_{17}\text{H}_{21}\text{O}_5\text{Cl}$, m.p. 180°, not hydrolysed when boiled for 4 hr. with aq.-alcoholic $\text{N-H}_2\text{SO}_4$ or for 7 hr. with 0.5N-NaOH. (I), (II), and (III) in COMe_2 with KMnO_4 give 3-chloro-2-hydroxy-4:6-dimethoxybenzoic acid, m.p. 224° (decomp.) (with CH_2N_2 this gives Me 3-chloro-2:4:6-trimethoxybenzoate), and a monobasic dimethoxy-acid, $\text{C}_{14}\text{H}_{15}\text{O}_5\text{Cl}$, m.p. 200° (decomp.), $[\alpha]_{\text{D}}^{25} -24^\circ$ as Na salt in 20% aq. MeOH, from which Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 37° for several days eliminates H_2O , producing the neutral substance, $\text{C}_{14}\text{H}_{13}\text{O}_5\text{Cl}$, m.p. 220°. (I) with KOH at 225—250° for 1 hr. gives orcinol. When the KCl of the medium is replaced by KBr no metabolic product containing Br is obtained although growth of the micro-organism occurs. When the medium for the isolation of fulvic acid is used no (I) is obtained.

W. McC.

Condensation product of 5-methylcoumaranone. W. BAKER and R. BANKS (J.C.S., 1939, 279—280).—5-Methylcoumaranone and Na give a bimol. compound, isolated as 3-acetoxy-5:5'-dimethyl-2:3'-dicoumaronyl, m.p. 127°, which with AcOH-HCl affords *s-tris-5-methyl-2:3-coumaronobenzene*, m.p. $>440^\circ$ (mol. wt. determination). F. R. S.

Syntheses of furanochromones and furanoflavones. B. L. MANJUNATH and E. SEETHARAMIAH (Ber., 1939, 72, [B], 97—100).—3-Hydroxy-4-methoxyacetylbenzofuran (I) is converted by Ac_2O and NaOAc at 165—170° into 3-methoxy-2-methyl-2':3'-7:8-furanochromone, m.p. 154.5°, converted by HI (d 1.7) in Ac_2O at 140° into 2-methyl-2':3'-7:8-furanochromonol, m.p. 240—242°. Similarly (I), (CHPh:CH-CO) $_2\text{O}$, and $\text{CHPh:CH-CO}_2\text{Na}$ at 180—190° yield 3-methoxy-2-styryl-2':3'-7:8-furanochromone, m.p. 173°, whence 2- β -phenylethyl-2':3'-7:8-furanochromonol, m.p. 154—156°. (I), anisic anhydride, and Na anisate afford 3:4'-dimethoxy-2':3'-7:8-furanoflavone, m.p. 166—168°, reduced to 4'-hydroxy-2':3'-7:8-furanoflavanol, gradual decomp. 271—282° after

softening at 271°, converted by boiling Ac_2O containing a trace of $\text{C}_5\text{H}_5\text{N}$ into the diacetate, m.p. 164—166°. Similarly, veratric anhydride gives 3:3':4'-trimethoxy-2':3'-7:8-furanoflavone, m.p. 184°, and 3':4'-dihydroxy-2':3'-7:8-furanoflavanol, decomp. 282—299° after softening at 282° in a sealed capillary (*Ac* derivative, m.p. 176—178°), and trimethylgallic anhydride affords 3:3':4':5'-tetramethoxy-2':3'-7:8-furanoflavone, m.p. 158—159°, whence 3':4':5'-trihydroxy-2':3'-7:8-furanoflavanol, decomp. 315° [*Ac* derivative, m.p. 234—236° (decomp.)]. H. W.

Crystalline solvates of inactive deguelin. L. D. GOODHUE and H. L. HALLER (J. Amer. Chem. Soc., 1939, 61, 486—488).—Deguelin (modified prep. from "cubé") forms solvates with 1 mol. of CHBr_3 , CCl_4 , CHCl_3 , or $(\text{CH}_2\text{Br})_2$ and with 0.5 mol. of PhCHO , PhBr , or PhCl . R. S. C.

Constituents of derris root. I. T. M. MEYER and D. R. KOOLHAAS (Rec. trav. chim., 1939, 58, 207—217).—A ketone ("derride"), $\text{C}_{18}\text{H}_{10}\text{O}_4(\text{OMe})_2$, m.p. 162—163°, $[\alpha]_{\text{D}} -19^\circ$ in C_6H_6 , $+13.7^\circ$ in COMe_2 (*oxime*, m.p. 240°), isomeric with the compound, m.p. 183°, of Buckley (B., 1936, 1117), has been isolated from the Et_2O extract of derris root. Derride gives no colour with FeCl_3 , is not dehydrated by $\text{AcOH-H}_2\text{SO}_4$, and when boiled with NaOAc and I in EtOH gives the same dehydrocompound as that of Buckley's product, together with a substance, m.p. 176°, resolidifying and remelting at 252°. Derride probably has the structure of isorotenone, but without the Pr^2 . The Et_2O extract of Sumatra derris root contains sumatrol, *l*- α -toxicarol, and a substance, $\text{C}_{20}\text{H}_{18}\text{O}_7$, m.p. 244°, $[\alpha]_{\text{D}} +107^\circ$ in C_6H_6 , $+189.1^\circ$ in COMe_2 , resembling toxicarol; the appended structure is suggested. A. Li.

Self-condensation of ethyl methylenebisthiacetate. New method for the preparation of derivatives of 1:3-dithian. F. CHALLENGER and S. A. MILLER (J.C.S., 1939, 347—348).—Self-condensation of Et methylenebisthiacetate gives Et 1:3-dithian-5-one-4-carboxylate, m.p. 62° (2:4-dinitrophenylhydrazone, m.p. 147°), hydrolysed to methylenebisthiacetic acid (Fe^{III} salt). F. R. S.

Piperidine derivatives.—See B., 1939, 243.

Dimorphism of dipyridine cobaltous chloride. D. P. MELLOR and B. S. MORRIS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 536—539).—The mol. wt. of the violet (I) and blue (II) form of dipyridine Co^{II} chloride is identical in CHBr_3 and in this solvent both forms have the same absorption spectrum and neither is a conductor at room temp. or during heating of the solution to 135°. In MeOH and H_2O (I) and (II) form pink solutions. The mol. conductivity of 0.0002N. solutions of (I) and (II) in EtOH is $320\Omega^{-1}$. This and the instantaneous and complete pptn. of AgCl on treating alcoholic solutions with AgNO_3 indicate that the substances can function as salts as well as nonelectrolytes. The evidence favours the view that (I) and (II) are dimorphous and that it is unnecessary to

postulate *cis-trans* isomerism of square co-ordinated Co^{II} to explain their occurrence. H. W.

Pyridinium salts.—See B., 1939, 245, 247.

Pyridine-3-carboxydiethylamide [nicotindieethylamide]. Its detection in "Cormed." G. BAUMGARTEN (Arch. Pharm., 1939, 277, 86—91).—This amide is identified in the prep. "Cormed" by its derivatives, $\text{C}_{22}\text{H}_{28}\text{O}_2\text{N}_6\text{S}_2\text{Cu}$ [prep. from $\text{Cu}(\text{CNS})_2$], softens at $165\text{--}170^\circ$, decomp. 180° , and $3[\text{Cu}(\text{CNS})_2] \cdot 4(\text{C}_{10}\text{H}_{14}\text{ON}_2)$. R. S. C.

Oxidative degradation of adermin. R. KUHN and G. WENDT (Ber., 1939, 72, [B], 305—309; cf. A., 1938, II, 373).—Adermin Me ether (I) is unchanged by $\text{Pb}(\text{OAc})_4$ in AcOH at 60° ; it is therefore not an α -glycol. Oxidation of vitamin- B_6 hydrochloride by 5N-CrO_3 in H_2SO_4 gives 0.86 mol. of AcOH . KMnO_4 (0 = 2) oxidises (I) in neutral aq. solution at 20° to a lactone (II), $\text{C}_9\text{H}_9\text{O}_3\text{N}$, m.p. 108° . With KMnO_4 (0 = 7) in alkaline solution (I) gives 3-methoxypyridine-4:5:6- or -2:4:5-tricarboxylic acid, anhydridised with loss of CO_2 to 3-methoxypyridine-4:5-dicarboxylic anhydride, m.p. 158° (Berl). The absorption spectrum of adermin (III) in 0.1N-HCl or 0.1N-NaOH is very similar to that of 3-hydroxypyridine and differs considerably from that of the 2- and 4-OH-compounds. A reversible displacement of the absorption spectrum by alkali is not observed. With the Folin-Denis reagent (III) gives a dark blue colour whereas (I) does not react. 3-Hydroxy- and 3-hydroxy-5-methyl-pyridine and 3-hydroxypyridine-5-carboxylic acid show the reaction, which is not given by 2-hydroxy-, 2-hydroxy-4:6-dimethyl-, 2:4-dihydroxy-6-methyl-3-ethyl-, 4-hydroxy-2:6-dimethyl-pyridine, or by 2-hydroxypyridine-5-carboxylic acid. The production of (II) proves that the $\text{CH}_2\text{-OH}$ of (III) are vicinal to one another. (III) is therefore 3-hydroxy-2-methyl-4:5-dihydroxymethyl-, -6-methyl-4:5-dihydroxymethyl-, or -4-methyl-5:6-dihydroxymethyl-pyridine. H. W.

Vitamin- B_6 , a derivative of 3-hydroxypyridine. R. KUHN, H. ANDERSAG, K. WESTPHAL, and G. WENDT (Ber., 1939, 72, [B], 309—310).—The synthesis of 3-methoxypyridine-4:5-dicarboxylic anhydride, m.p. 158° , identical with that derived from adermin (I), is announced but not described. Partial oxidation of adermin Me ether gives a methyl-3-methoxypyridinedicarboxylic acid which gives an anhydride which does not yield a colour with $\text{FeSO}_4 \cdot \text{CH}_2\text{-OH}$ cannot therefore be attributed to $\text{C}_{(2)}$ or $\text{C}_{(6)}$, and (I) is therefore 3-hydroxy-2-methyl-4:5-dihydroxymethyl- or -6-methyl-4:5-dihydroxymethyl-pyridine. H. W.

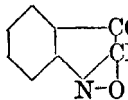
Constitution of adermin. R. KUHN, G. WENDT, and K. WESTPHAL (Ber., 1939, 72, [B], 310—311).—Oxidation of adermin Me ether with $\text{Ba}(\text{MnO}_4)_2$ gives a methoxymethylpyridinedicarboxylic acid (+1.5 H_2O) which does not contain CO_2H at $\text{C}_{(2)}$ or $\text{C}_{(6)}$, since it does not give a colour with FeSO_4 . It is converted by hot Ac_2O into an anhydride, m.p. 64° , identified by comparison with synthetic 3-methoxy-2-methylpyridine-4:5-dicarboxylic anhydride. Adermin is therefore 3-hydroxy-2-methyl-4:5-dihydroxymethyl-pyridine. H. W.

Re-conversion of adermin methyl ether into adermin. R. KUHN and G. WENDT (Ber., 1939, 72, [B], 311—312).—Adermin Me ether is transformed by boiling 66% HBr into 3-hydroxy-2-methyl-4:5-dibromomethylpyridine hydrobromide, m.p. 217° (decomp.), which gives a dark blue colour with the Folin-Denis reagent and couples with diazotised $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-SO}_3\text{H}$ to an orange dye. It is converted by AgOAc in boiling H_2O followed by HCl into adermin hydrochloride, m.p. $200\text{--}201^\circ$, whence the free base, m.p. 159° . Adermin hydrobromide has m.p. 193° (decomp.). H. W.

Indolines.—See B., 1939, 248.

6:8-Dichlorobenzoylenecarbamide and the interaction of 5:7-dihalogenoisatoic anhydrides with ammonia. New reagent for sodium. F. E. SHEIBLEY (J. Org. Chem., 1938, 3, 414—423; cf. A., 1934, 307).—2:3:5:1-NH $_2$ · $\text{C}_6\text{H}_2\text{Cl}_2$ · CO_2H (I) is transformed by $\text{CO}(\text{NH}_2)_2$ at 140° into 6:8-dichlorobenzoylenecarbamide [6:8-dibromo-2:4-diketo-1:2:3:4-tetrahydroquinazoline] (II), m.p. 296° (corr.) after softening and undergoing an apparent change of cryst. form $\sim 280^\circ$, and 3:5-dichloro-2-aminobenzamide, m.p. 182.5° (corr.), which is possibly an intermediate since it yields (II) when heated with $\text{CO}(\text{NH}_2)_2$ at $160\text{--}165^\circ$. (II) dissolved in KOH is a useful reagent for Na , with which it gives a ppt., $\text{C}_6\text{H}_3\text{O}_2\text{N}_2\text{Cl}_2\text{Na} \cdot 1.5\text{H}_2\text{O}$. Boiling ClCO_2Et and (I) give a substance, m.p. $\sim 220^\circ$, and 5:7-dichloroisatoic anhydride (III), m.p. 261° (corr.; decomp.), also obtained by oxidation of tetrachloroindigotin by CrO_3 in AcOH . 5:7-Dibromoisatoic anhydride (IV), m.p. 263.5° (corr.; decomp.), is obtained analogously from tetrabromoindigotin. 28% NH_3 at 100° transforms (III) into (II) and (I). (IV) behaves similarly. H. W.

Heterocyclic compounds containing nitrogen. XXXVI. Preparation from *oo'*-dinitrotolan of a vat dye containing chlorine. P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1939, 22, 134—139; cf. A., 1938, II, 460).—Chlorination of 2:2'-dinitrostilbene in AcOH in the light of an arc lamp gives mainly the normal dichloride with some red 2-(3':5'-dichloro-2'-nitrophenyl)isatogen, $\text{C}_6\text{H}_4\text{<CO>CR}$ ($\text{R} = 3:5:2\text{-C}_6\text{H}_2\text{Cl}_2\text{NO}_2$) (I), m.p. $185\text{--}186^\circ$. The yellow substance, m.p. 177° (Ruggli *et al.*, A., 1938, II, 437), obtained by the action of NaI in COMe_2 on β -dichloro- α -keto- α -2-nitrosophenyl- β -3':5'-dichloro-6'-nitrophenylethane is identified as 2-(3':5'-dichloro-2'-nitrophenyl)isatogen (II); it is also obtained by isomerisation of (I) by EtOH -conc. HCl . It is stable towards halogen and only slowly attacked by $\text{KMnO}_4\text{-Na}_2\text{CO}_3$. $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ and an acid, m.p. 225° , in small amount are the sole cryst. products of its oxidation. Reduction of (II) with SnCl_2 in AcOH-HCl gives a canary-yellow compound, $\text{C}_{14}\text{H}_6\text{O}_2\text{N}_2\text{Cl}_2$, m.p. $224\text{--}225^\circ$, and a red-brown substance, $\text{C}_{14}\text{H}_8\text{ON}_2\text{Cl}_2$, m.p. 236° , which possibly belong to the di-indole series. Complete reduction of (II) ($\text{H}_2\text{-Ni}$; NPh-NH_2 ; Zn dust and AcOH) affords a vat which on exposure to air after addition of NH_3 deposits 3:5'-dichloro-2'-



(II.)

aminophenylindolone, $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ N \end{smallmatrix} > C \cdot C_6H_4Cl_2 \cdot NH_2$, m.p. 203—204° (slight decomp.) (*semicarbazone*), best obtained by direct catalytic hydrogenation of (II).

H. W.

Heterocyclic compounds containing nitrogen.
XXXVIII. isolsatogens. P. RUGGLI, E. CASPAR, and B. HEGEDŰS (Helv. Chim. Acta, 1939, 22, 140—146).—The best reagent for the isomerisation of 6-carbethoxy-2-phenylisatogen (A., 1919, i, 221) to 6-carbethoxy-2-phenylisatogen (I), m.p. 100·5°, is H_2SO_4 -EtOH, which also slowly transforms 2-phenylisatogen (II) into 2-phenylisatogen (III), m.p. 94°. (I) is reduced by Zn dust and warm AcOH to 6-carbethoxy-2-phenylindoxyl and does not appear to react with CH_2N_2 . (III) dissolves in CH_2N_2 -Et₂O without evolution of gas and is recovered mixed with some resin when the solution is evaporated. Reduction of (II) with Zn dust and AcOH gives the additive product of phenylindoxyl and phenylindolone whilst catalytic reduction (Raney Ni in Ac₂O at room temp.) leads to acetyl-2-phenylindoxyl. Oximation of (II) gives 15% of the C-oxime and 37% of the N-oxime (IV). Similar treatment of (III) gives a small amount of 2-phenylindoloneoxime obviously due to a reducing action of the NH_2OH salt. The sole main product of the change appears to be (IV). PhNCO does not appear to react with (II) or (III).

H. W.

Heterocyclic compounds containing nitrogen.
XXXIX. Reduction of o-nitrobenzil and a further synthesis of 2-phenylisatogen. P. RUGGLI and B. HEGEDŰS (Helv. Chim. Acta, 1939, 22, 147—150).—Oxidation of o-nitrotolan with a considerable excess of CrO_3 in AcOH gives o-nitrobenzil (I), m.p. 100°. Interruption of the catalytic hydrogenation (Raney Ni in moist EtOAc) after absorption of 3 H gives 2-phenylisatogen in 34% yield which diminishes to 10% after absorption of 6 H. Hydrogenation in Ac₂O permits the isolation of the immediately formed o-hydroxylaminobenzil as its Ac derivative, o-COBz·C₆H₄·NAc·OH, m.p. 169—171° (decomp.) after incipient reddening at 165°. Reduction of (I) with Zn dust and AcOH affords exclusively the substance, $(C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ NH \end{smallmatrix} > CPh)_2O$.

H. W.

Isatindiresorcinol (tetrahydroxydiphenyloxindole) and some derivatives. E. BUREŠ and J. HRABOVÁ (Coll. Czech. Chem. Comm., 1939, 11, 39—46).—Isatin and resorcinol with $ZnCl_2$ at 115°, or when treated in H_2O with conc. H_2SO_4 , yield tetrahydroxydiphenyloxindole (I), which gives with Br in AcOH, Br_2 - and Br_4 -compounds, with I in aq. KI-KOH, a I_2 -, and with Cl_2 in AcOH, a Cl_3 -compound (II). Condensation (conc. H_2SO_4) of isatin with resorcinol, and bromination of the product, yields a tetrabromodisulphonic acid (III) of (I). The Li, Na, and K derivatives of all these phenols, and the Sb derivatives (solution in aq. NaOH treated with K antimonyl tartrate) of all except (II) and (III), have been prepared.

A. LI.

Indoles. IV. Utilisation of the Japp-Klingemann reaction for the preparation of substituted indolecarboxylic acids. G. K. HUGHES and F. LIONS [with, in part, J. G. MCKEAN, A. J. MURRAY,

V. CALLANAN, D. H. FREEMAN, C. S. RALPH, R. RASSACK, J. DOMBROSKI, F. FINCH, R. ANDREWS, R. C. BETTY, R. H. SCOTT, C. W. VERNON, A. FLACK, and C. H. LAURENCE] (J. Proc. Roy. Soc. New South Wales, 1938, 71, 475—485; cf. A., 1933, 835).—The substituted phenylhydrazones of Et α-acetylpropionate, α-acetylbutyrate, α-acetylhexoate, and α-acetyl-β-phenylpropionate are obtained by use of the requisite diazonium chloride. These are cyclised by dry HCl in abs. EtOH and the indole esters are hydrolysed by KOH. The following compounds are described: (from α-C₁₀H₇NH₂) Et pyruvate-1-naphthylhydrazone, m.p. 125°; Et 6:7-benzindole-8-carboxylate, m.p. 170° (acid, m.p. 204—205°); Et 7-methyl-6:7-benzindole-8-carboxylate, m.p. 176°; Et 7-n-propyl-5:6-benzindole-8-carboxylate, m.p. 185—186° (acid, m.p. 182—183°); Et 7-phenyl-5:6-benzindole-8-carboxylate, m.p. 187°; (from β-C₁₀H₇NH₂) Et 4:5-benzindole-2-carboxylate, m.p. 161° (acid, m.p. 160°); Et 1-methyl-4:5-benzindole-2-carboxylate, m.p. 176° (acid, m.p. 176°); Et 1-phenyl-4:5-benzindole-2-carboxylate, m.p. 179° (acid, m.p. 201°); (from o-OEt·C₆H₄NH₂) Et 7-ethoxyindole-2-carboxylate, b.p. 170—175°/2 mm., m.p. 160°; Et 7-ethoxy-3-n-propylindole-2-carboxylate, b.p. 177°/2 mm. (acid, m.p. 162°); Et 7-ethoxy-3-phenylindole-2-carboxylate, b.p. 216—224°/2 mm., m.p. 93° (acid, m.p. 206—207°); (from p-OEt·C₆H₄NH₂) Et 5-ethoxyindole-2-carboxylate, m.p. 155—156°; Et 5-ethoxy-3-methylindole-2-carboxylate, m.p. 167° (acid, m.p. 178°); Et 5-ethoxy-3-n-propylindole-2-carboxylate, m.p. 142° (acid, m.p. 178°); Et 5-ethoxy-3-phenylindole-2-carboxylate, m.p. 148—149° (acid, m.p. 183—185°); (from p-OMe·C₆H₄NH₂) Et 5-methoxyindole-2-carboxylate, m.p. 152—153°; Et 5-methoxy-3-methyl-, m.p. 146—147°, -3-n-propyl-, m.p. 106°, -2-phenyl-, m.p. 121—122°, -indole-2-carboxylate; (from p-C₆H₄Br·NH₂) Et 5-bromoindole-2-carboxylate, m.p. 153° [acid, m.p. 188° (decomp.)]; Et 5-bromo-3-methylindole-2-carboxylate, m.p. 163° (acid, m.p. 217—218°); Et 5-bromo-3-n-propylindole-2-carboxylate, m.p. 149° (acid, m.p. 160°); Et 5-bromo-3-phenylindole-2-carboxylate, m.p. 185° (acid, m.p. 216°); (from p-NH₂·C₆H₄·CO₂Et) Et pyruvate-p-carbethoxyphenylhydrazone, m.p. 137°, unaffected by HCl or by boiling AcOH; Et α-ketobutyrate-p-carbethoxyphenylhydrazone, m.p. 141°; Et 5-carbethoxy-3-methylindole-2-carboxylate, m.p. 181°, and 3-methylindole-2:5-dicarboxylic acid, m.p. 298°; Et 3-n-propylindole-2:5-dicarboxylate, m.p. 133—134° (dibasic acid, m.p. 282°); Et 3-phenylindole-2:5-dicarboxylate, m.p. 196—197° (dibasic acid, m.p. 290° after softening at 270°).

H. W.

Indoles. VI. Application of the Fischer synthesis to some cyclohexyl ketones. G. K. HUGHES and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 494—502).—cycloHexyl Me ketone (dinitrophenylhydrazone, m.p. 128°) and NHPh·NH₂ give a non-cryst. phenylhydrazone, transformed by boiling AcOH into 1-cyclohexane-3-2-methylindoleninespiran $N \begin{smallmatrix} C_6H_4 \\ \diagup \diagdown \\ CMe \end{smallmatrix} > C \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagup \diagdown \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH_2$, b.p. 131—134°/2 mm. [picrate, m.p. 188°; methiodide (I), m.p. 248°; ethiodide, m.p. 252°]. (I), CH(OEt)₂, and anhyd. C₂H₅N at 100° yield 3:3'-di(cyclohexanespiran)-1:1'-dimethylindocarbocyanine, m.p. 265°; the corresponding

1:1'-Et₂ compound has m.p. 265°. (I) and *p*-NMe₂·C₆H₄·CHO in boiling MeOH afford 1-cyclohexane-3-2-*p*-dimethylaminostyrylindoleninespiran methiodide, m.p. 241°, whereas *p*-dimethylaminobenzylidenedi-2-methyl-3-cyclohexanespiranindolenine methiodide, m.p. 248°, is obtained from the same reactants in other proportions. Anisole, cyclohexanecarboxyl chloride, and AlCl₃ in CS₂ give cyclohexyl *p*-anisyl ketone, b.p. 206–208°/26 mm., m.p. 66° (dinitrophenylhydrazone, m.p. 123°), the phenylhydrazone, m.p. 120°, of which passes in boiling glacial AcOH into 1-cyclohexane-3-2-*p*-anisylindoleninespiran, b.p. 205–210°/1.2 mm., m.p. 107° (picrate, m.p. 211°; methiodide, m.p. 156°). Similarly the non-cryst. phenylhydrazone of cyclohexyl Ph ketone is converted into 1-cyclohexane-3-2-phenylindoleninespiran, b.p. 195–200°/1.5 mm., m.p. 86° (picrate, m.p. 170°; methiodide, m.p. 204°). cycloHexyl Ph ketone dinitrophenylhydrazone has m.p. 192°. cycloHexyl veratryl ketone, b.p. 221–223°/20 mm., m.p. 51° (dinitrophenylhydrazone, m.p. 147°), yields a phenylhydrazone, m.p. 190°, transformed by AcOH into 1-cyclohexane-3-2-veratrylindoleninespiran, m.p. 152° (picrate, m.p. 217°; methiodide, m.p. 207°). H. W.

Syntheses in the series of chemotherapeutically active derivatives of sulphanilamide. B. BOBRANSKI (Arch. Pharm., 1939, 277, 75–86).—2- and 4-Chloroquinoline and *p*-NH₂·C₆H₄·SO₂·NH₂ at 170–180° give *p*-2-, m.p. 251° (hydrochloride, m.p. 264°), and *p*-4-quinolylaminobenzenesulphonamide, m.p. 262–263° [hydrochloride, m.p. 311° (decomp.); sinters at 300°]. *p*-NHAc·C₆H₄·SO₂Cl and the appropriate aminoquinoline in hot C₅H₅N give 5-, m.p. 258° (decomp.), 6-, m.p. 282° (decomp.), 7-, m.p. 238°, and 8-*p*-acetylaminobenzenesulphonamidoquinoline, m.p. 193°, hydrolysed by 15% HCl to the *p*-aminobenzenesulphonamidoquinolines, m.p. 230°, 201°, 206°, and 193.5°, respectively. R. S. C.

Quinoline derivatives [trypanocides].—See B., 1939, 326.

Antimalarials. I. Derivatives of 4-acetoacetyl-6-methoxyquinoline. W. H. LINNELL and W. RIGBY (Quart. J. Pharm., 1938, 11, 722–728).—Et quinate with COMe₂·NaOEt affords 4-acetoacetyl-6-methoxyquinoline (I) [two cryst. forms (?), m.p. 90° and 99°] [oxime, m.p. 182° (corr.), converted by HCl-Et₂O into 5-(7'-methoxy-4'-quinolyl)-3-methylisooxazole, m.p. 92–93° (corr.) (phenylhydrazone, m.p. 171–172°), converted by dil. HCl into 1-phenyl-5-(7'-methoxy-4'-quinolyl)-3-methylpyrazole, m.p. 94° (corr.)]. (I) with NH₃ yields 6-methoxy-4-(Δ^β-α-keto-γ-aminobutenyl)quinoline, m.p. 253–255°, and with bornylamine, 6-methoxy-4-(Δ^β-α-keto-γ-bornylaminobutenyl)quinoline, m.p. 110° (corr.). F. O. H.

Abrin naphthalene-2-sulphonate, m.p. 192–194°, flavianate, decomp. 195°, picrolonate, decomp. 285–286°, and phosphotungstate.—See A., 1939, III, 296.

aci-Nitrobetaines. F. KRÖHNKE and H. SCHMEISS (Ber., 1939, 72, [B], 440–445; cf. A., 1937, II, 208).—2:4-(NO₂)₂C₆H₃·CH₂Cl is converted by C₅H₅N in EtOH at 100° into 2:4-dinitrobenzylpyridinium chloride (I), decomp. >190° (corresponding perchlorate,

m.p. 160–161°), also obtained less advantageously by the prolonged hydrolysis of ω-2:4-dinitrophenylphenacylpyridinium enol betaine. *N*-NaOH transforms (I) into the corresponding nitrobetaine, m.p. 124–126°, which is regarded, on account of its dark colour and its ability to condense with *p*-NO₂·C₆H₄·NMe₂ in EtOH containing piperidine to 2:4-dinitrophenyl-*N*-4'-dimethylaminophenylnitron, m.p. 198° (decomp.), as a mesomeric equilibrium mixture of the aci- and the carbenate zwitterion forms. 2:4-Dinitrobenzylisoquinolinium chloride, m.p. 180°, is converted by alkali into a very unstable, blue, amorphous product. 2:4:6-Trinitrobenzylpyridinium chloride, m.p. 140–141° (decomp.) (corresponding perchlorate, decomp. >210°), obtained by the action of hot, conc. HCl on ω-trinitrophenylphenacylpyridinium enol betaine, is converted by 0.1*N*-NaOH or aq. NH₄Et₂ into the acinitrobetaine, decomp. ~140° according to the rate of heating. 5-Chloro-2:4-dinitrobenzylpyridinium chloride, decomp. ~190° (corresponding perchlorate, m.p. 174–175°), yields a moderately stable betaine C₁₂H₈O₄N₃Cl, slow decomp. ~150°. 1:3:5-C₆H₃Me(NO₂)₂ and Br at 110° give 3:5-dinitrobenzyl bromide, b.p. 177°/0.3 mm., m.p. 65–66°, converted by C₅H₅N in EtOH at 100° into 3:5-dinitrobenzylpyridinium bromide, m.p. 273–274° (corresponding perchlorate, m.p. 191–192°), whence is derived 3:5-dinitrophenyl-*N*-4'-dimethylaminophenylnitron, m.p. 239° (decomp.) (or, in an individual case, a substance, m.p. 191°), hydrolysed by 5*N*-H₂SO₄ to 3:5-(NO₂)₂C₆H₃·CHO, *p*-Nitrodiphenylmethylpyridinium perchlorate, m.p. 133°, yields the corresponding dimethylaminophenylnitron, decomp. ~155°, hydrolysed to *p*-C₆H₄Br₃·NO₂.

H. W.

Heterocyclic compounds derived from pyrocatechol ethers. I. Derivatives of 6:7-dimethoxyquinoline. F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 242–250).—4-Aminoveratrole (I) is converted by paracetaldehyde in presence of conc. HCl and ZnCl₂ into 6:7-dimethoxy-2-methylquinoline, b.p. 195–200°/4 mm., m.p. 103° (methiodide, m.p. 241°; ethiodide). CH₂Ac·CO₂Et and (I) in presence of a little 5*N*-HCl afford Et β-3:4-dimethoxyanilinocrotonate, m.p. 61°, readily cyclised in paraffin oil at 270° to 4-hydroxy-6:7-dimethoxy-2-methylquinoline, m.p. 280°. Similarly 3:4:1-(OEt)₂C₆H₃·NH₂, CH₂Ac·CO₂Et, and a little HCl yield non-cryst. Et β-3:4-diethoxyanilinocrotonate, cyclised at 280° to 4-hydroxy-6:7-diethoxy-2-methylquinoline, m.p. 211°. CH₂Ac·CO₂Et and (I) at 160° give 4-acetamidoveratrole, m.p. 59°, transformed by cold, conc. H₂SO₄ into 2-hydroxy-6:7-dimethoxy-4-methylquinoline, m.p. 235°. Et cyclohexanone-2-carboxylate and (I) in presence of 5*N*-HCl afford Et 2-3':4'-dimethoxyanilino-Δ¹-cyclohexene-1-carboxylate, m.p. 72° (yield 90–95%), which passes in paraffin at 270° into 5-hydroxy-7:8-dimethoxy-1:2:3:4-tetrahydroacridine, m.p. >300° (hydrochloride, m.p. 244°). Similarly, 3:4:1-(OEt)₂C₆H₃·NH₂ gives successively Et 2-3':4'-diethoxyanilino-Δ¹-cyclohexene-1-carboxylate, m.p. 44°, and 5-hydroxy-7:8-diethoxy-1:2:3:4-tetrahydroacridine, m.p. 281°. CH₂AcBz and (I) in presence of a little 5*N*-HCl yield Ph β-3:4-dimethoxyanilino-Δ¹-

propenyl ketone, m.p. 100°, in nearly quant. yield; it is converted by cold, conc. H_2SO_4 into 6 : 7-dimethoxy-4-phenyl-2-methylquinoline, m.p. 142°. H. W.

Heterocyclic compounds derived from pyrocatechol ethers. II. 7 : 8-Dimethoxy- and 5 : 6 : 7-trimethoxy-quinolines. J. N. GRAVES, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 251—254).—3-Aminoveratrole (I), $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and 5N-HCl at room temp. yield the non-cryst. Et β -2 : 3-dimethoxyanilinocrotonate, which passes in paraffin at 280° into 4-hydroxy-7 : 8-dimethoxy-2-methylquinoline, m.p. 212° (picrate, m.p. 230°). (I) is transformed by the successive action of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ at 145° and conc. H_2SO_4 at 0° into 2-hydroxy-7 : 8-dimethoxy-4-methylquinoline, m.p. 175°. Et cyclohexanone-2-carboxylate (II), (I), and 5N-HCl at room temp. give a non-cryst. product which passes at 280° into 5-hydroxy-8 : 9-dimethoxy-1 : 2 : 3 : 4-tetrahydroacridine, m.p. 212° (decomp.) (picrate, m.p. 158°). 5-Aminopyrogallol Me_3 ether (III), $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and 5N-HCl yield an oil which passes at 280° into 4-hydroxy-5 : 6 : 7-trimethoxy-2-methylquinoline, m.p. 198°. 2-Hydroxy-5 : 6 : 7-trimethoxy-4-methylquinoline, m.p. 218° (picrate, m.p. 180°), is obtained by treating (III) with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ at 140° and then with conc. H_2SO_4 at 0°. 5-Hydroxy-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydroacridine, m.p. 200°, is obtained by treating (II) and (III) with 5N-HCl and heating the product at 280°. Attempts to prepare 1-carboxy-2 : 3-dimethoxyphenylthiolacetic acid by diazotising 2-aminoveratric acid (IV) and adding $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ to the solution gave only unchanged (IV). H. W.

isoQuinoline compounds. I. P. K. PAUL (Science & Culture, 1936, 1, 781).—Gallic acid Me_3 ether and CH_2O yield a chloromethylphthalide which with KCN affords the *cyanomethylphthalide* derivative, m.p. 146°, hydrolysed (10% NaOH) to a $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ derivative, m.p. 212°, the chloride of which with β -veratrylethylamine gives the substituted *amide*, m.p. 154°; the last is cyclised with POCl_3 to an *isoquinoline* derivative, m.p. 183° (hydrochloride, m.p. 208°), with the emetine skeleton. CH. ABS. (c)

Heterocyclic compounds derived from pyrocatechol ethers. V. Synthesis of 2 : 3 : 6 : 7-tetramethoxycarbazole and some dimethoxycarbazoles. G. K. HUGHES, F. LIONS, J. J. MAUNSELL, and L. E. A. WRIGHT (J. Proc. Roy. Soc. New South Wales, 1938, 71, 428—434).—Gradual addition of Cu powder to 4-bromo-5-nitroveratrole (I) at 210—225° and subsequent heating of the mixture at 240° gives 2 : 2'-dinitro-4 : 5 : 4' : 5'-tetramethoxydiphenyl, m.p. 218°, reduced by Zn dust and AcOH at 70° to 2 : 2'-diamino-4 : 5 : 4' : 5'-tetramethoxydiphenyl, m.p. 180° [picrate, m.p. 226° (decomp.)], which is demethylated and extensively decomposed by hot dil. acids but is transformed by tetrazotisation and treatment with K_2S into 2 : 3 : 6 : 7-tetramethoxycarbazole, m.p. 212°. NH_2Ph (I) and anhyd. NaOAc at 200—210° afford 2-nitro-4 : 5-dimethoxydiphenylamine, m.p. 91°, little affected by Zn dust and AcOH or by SnCl_2 but reduced by Sn -conc. HCl-EtOH to 2-amino-4 : 5-dimethoxydiphenylamine, m.p. 152°. This is transformed by HNO_2 at 0° into 5 : 6-dimethoxy-

1-phenylbenztriazole, m.p. 128°, which passes at 300°/partial vac. into 2 : 3-dimethoxycarbazole, b.p. 255—260°/25 mm., m.p. 125°. Addition of 2-chlorocyclohexanone to a mixture of 4-aminoveratrole and anhyd. NaOAc which is then heated to 170° yields 2 : 3-dimethoxy-5 : 6 : 7 : 8-tetrahydrocarbazole, b.p. 255—260°/25 mm., m.p. 98°, slowly converted by boiling Ac_2O into 9-acetyl-2 : 3-dimethoxy-5 : 6 : 7 : 8-tetrahydrocarbazole, b.p. 220°/2 mm., m.p. 136°.

H. W.

Structural problems in the indole group. III. Halogen compounds. S. G. P. PLANT and (Miss) A. E. J. WILSON (J.C.S., 1939, 237—239).—4 : 2- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ and cyclohexanone give (H $_2\text{SO}_4$) 5-chlorotetrahydrocarbazole-8-carboxylic acid, m.p. 245° (decomp.), which, after acetylation and treatment with quinoline and Cu chromite, affords 5-chloro-9-acetyltetrahydrocarbazole. cycloHexanone and $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ with H_2SO_4 yield a mixture of 7-, m.p. 183° (decomp.) [9-Ac derivative (I), m.p. 123°], and 5-bromotetrahydrocarbazole (9-Ac derivative, m.p. 137—139°). HNO_3 converts (I) into 7-bromo-10 : 11-dihydroxy-9-acetylhexahydrocarbazole, m.p. 217° (decomp.), which with Ac_2O loses H_2O to form 8-bromo-6-acetyl- ψ -indozylspirocyclopentane, m.p. 107—108°. After removal of Ac, this compound is nitrated to 8-bromo-7 : 9-dinitro- ψ -indozylspirocyclopentane, m.p. 202°, which with NH_2Ph gives the 7 : 9-dinitro-8-anilino-compound (II), m.p. 235°. 7-Chloro-9-acetyltetrahydrocarbazole and HNO_3 yield 7-chloro-10 : 11-dihydroxy-9-acetylhexahydrocarbazole, m.p. 205—206°, which is converted by a similar series of reactions into (II). Treatment of 5-bromo-9-acetyltetrahydrocarbazole gives only 5-bromo-7-nitro-9-acetyltetrahydrocarbazole, m.p. 217°. F. R. S.

Heterocyclic compounds derived from pyrocatechol ethers. III. Synthesis of 1 : 2-dimethoxyacridine. J. N. GRAVES, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 255—258).—3-Aminoveratrole, $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$, Cu powder, and anhyd. K_2CO_3 in boiling amyl alcohol give 2 : 3-dimethoxydiphenylamine-2'-carboxylic acid (I), m.p. 162°. Gradual addition of Cu-bronze and anhyd. K_2CO_3 to 2-aminoveratric acid in boiling PhBr affords 2 : 3-dimethoxydiphenylamine-6-carboxylic acid (II), m.p. 155°. PCl_5 in boiling CS_2 cyclises (I) and (II) to 1 : 2-dimethoxyacridone, m.p. 225°, reduced by Na and abs. EtOH to 1 : 2-dimethoxydihydroacridine, m.p. 218°, which shows a vivid blue fluorescence in EtOH and is oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$ -dil. H_2SO_4) to 1 : 2-dimethoxyacridine, m.p. 189° [picrate, m.p. 220° (decomp.)]. H. W.

Heterocyclic compounds derived from pyrocatechol ethers. IV. Syntheses of dimethoxybenzacrindines. G. K. HUGHES, F. LIONS, F. H. MONAGHAN, and T. WILKINSON (J. Proc. Roy. Soc. New South Wales, 1938, 71, 421—429).—4-Aminoveratrole (I) is converted by PhCHO at 100° into 4-benzylideneaminoveratrole (II), m.p. 71°, and by piperonal into 4-piperonylideneaminoveratrole (III), m.p. 107°. $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and (II) at 210° give 7 : 8-dimethoxy-5-phenyl-3 : 4-benzacrindine, m.p. 205° (hydrochloride; picrate, m.p. 289°; methiodide, m.p. 223°), and 7 : 8-dimethoxy-5-phenyl-5 : 10-dihydro-1 : 2-

benzacridine, m.p. 198° (Ac derivative, m.p. 228°). Similarly, (III) and β -C₁₀H₇·OH yield 6:7-dimethoxy-5-piperonyl-3:4-benzacridine, m.p. 245° (hydrochloride, m.p. 228°; picrate, decomp. 269°), and 6:7-dimethoxy-5-piperonyl-5:10-dihydro-1:2-benzacridine, m.p. 242° (Ac derivative, m.p. 258°). (I), its hydrochloride, and 40% CH₂O yield 2:2'-diamino-4:5:4':5'-tetramethoxydiphenylmethane, m.p. 140° [dihydrochloride, m.p. 220°; picrate, m.p. 190—195° (decomp.)]; Ac₂ derivative], which can be diazotised and coupled with β -C₁₀H₇·OH to a red dye; attempts to transform it into an acridine derivative were unsuccessful.

H. W.

Derivatives of 4-hydroxyquinoline. G. K. HUGHES and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 458—461).—Equimol. quantities of amine and β -keto-ester are mixed and in some cases gently heated on the water-bath. If the intermediate arylamino-ester crystallises it is filtered and purified. If not cryst. it is dissolved in Et₂O and the solvent is removed. The intermediates are cyclised by first warming at 100° and then adding them to liquid paraffin at 280°. The following *Et* arylamino- Δ^1 -cyclohexene-2-carboxylates are derived from *Et* cyclohexanone-2-carboxylate; *o*-toluidino-, m.p. 84°; *p*-bromoanilino-, m.p. 78°; *p*-xenylamino-, m.p. 107°; *o*-anisidino-, m.p. 80°; *p*-anisidino-, m.p. 71°; *p*-phenetidino-, m.p. 87°; *p*-carboxyanilino-, m.p. 166°; 3-acenaphtheneamino-, m.p. 122°. The following substituted tetrahydroacridines are described: 1-, m.p. >300°, and 3-methyl-, m.p. >300°; 1-, m.p. 278°, and 3-methoxy-, m.p. 284°; 1-, m.p. 237°, and 3-ethoxy-, m.p. >300°; 2:3-, m.p. >300°, and 3:4-benzo-, m.p. >300°; 1-, m.p. 200°, and 3-phenyl-, m.p. >300°; 3-nitro-, m.p. >300°; 3-bromo-, m.p. >300°; 1-, m.p. 260°, and 3-chloro-, m.p. >300°; 1:3-dichloro-, m.p. 296°; 3-carboxy-, m.p. >300°; 3-carbethoxy-, m.p. >300°; 3-acetamido-, m.p. >300°; compounds C₁₈H₁₇ON, m.p. >300°, and C₁₅H₁₁ON, m.p. 255°, from 3-aminoacenaphthene and *p*-xylidine respectively. The following 4-hydroxy-2-methylquinolines are described. 6-, m.p. >300°, and 7-bromo-, m.p. >300°; 8-phenyl-, m.p. 280°; 6-acetamido-, m.p. >300°; 8-chloro-, m.p. 220°; 6:8-dichloro-, m.p. 290°.

H. W.

Synthesis of pharmacologically important amines. XII. Di- and tetra-hydrobenzisoquinolines as protozoa-poisons. K. KINDLER, W. PESCHKE, and G. FLÜDDERMANN (Arch. Pharm., 1939, 277, 25—32; cf. A., 1936, 200).—Hydrogenation (Pd-C) of β -C₁₀H₇·CH₂·CN (prep. from 2-C₁₀H₇Me by way of 2-C₁₀H₇·CH₂Br) in H₂SO₄-AcOH at room temp./1 atm. gives 60% of 2-C₁₀H₇·[CH₂]₂·NH₂, b.p. 168—169°/19 mm., the Bz derivative, new m.p. 142—143°, of which with POCl₃ in boiling xylene gives 56% of 1-phenyl-3:4-dihydro-6:7-benzisoquinoline (I), m.p. 127—128°. The 3:4-diethoxybenzoyl derivative, m.p. 144—146°, gives similarly 1:3'-4'-diethoxyphenyl-3:4-dihydro-6:7-benzisoquinoline (II), m.p. 148—149°. 1-C₁₀H₇·CH₂·CN gives similarly 1-C₁₀H₇·[CH₂]₂·NH₂, b.p. 178—181°/20 mm. (Bz derivative, new m.p. 96°), and 1-phenyl-3:4-dihydro-5:6-benzisoquinoline (III), m.p. 78—80° (picrate, m.p. 200—202°). Hydrogenation (Pd-BaSO₄) of (I)

L (A., II.)

and (III) gives 1-phenyl-1:2:3:4-tetrahydro-6:7- (IV), m.p. 124—125° (and a by-product, m.p. 229—230°), and 5:6-benzisoquinoline (V), m.p. 103—104°, respectively. (I), (II), (III), (IV), and (V) are 2-4, 1-6, 2-0, 11-0, and 7-5 times, respectively, as effective as quinine against protozoa.

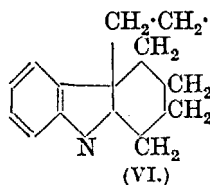
R. S. C.

Synthetic substances allied to strychnine. F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 192—208).—Et₂ α -acetyl- α -methylglutarate is hydrolysed by conc. HCl to γ -acetyl-*n*-valeric acid (I), b.p. 148—151°/11 mm. [semicarbazone, m.p. 159—162° (decomp.)]. This is converted by *o*-NH₂·C₆H₄·CHO and NaOH in EtOH into γ -2-quinolyl-*n*-valeric acid, m.p. 133°, transformed by successive treatments with Na-Hg and boiling HCl into γ -2-1:2:3:4-tetrahydroquinolyl-*n*-valeric anhydride (II), CH₂—C(CH₂)₂—CH(CHMe)—CH₂—C(CH₂)₂—N(CO)—CH₂, m.p. 80°, which in 60% H₂SO₄ gives a transient, deep purple coloration on addition of a little aq. K₂Cr₂O₇. Similarly isatin and (I) yield 4-carboxyquinolyl- γ -valeric acid, m.p. 248—249°, which loses CO₂ when heated above its m.p., giving an oil from which (II) cannot be isolated. Successive additions of *Et* cyclohexanone-2-carboxylate and CH₂Cl·CH₂·CO₂Et to KOEt-EtOH give *Et* 2-carbethoxycyclohexanone-2- β -propionate, b.p. 156—158°/2 mm., hydrolysed by HCl to cyclohexanone-2- β -propionic acid (III), b.p. 183—184°/12 mm., m.p. 62° (semicarbazone, m.p. 194° (decomp.)); *Et* (IV), b.p. 140—143°/12 mm., and *Me*, b.p. 133—134°/12 mm., esters]. cycloHexanone-2- β -propionamide, m.p. 162—163°, passes above its m.p. into 2-keto-1:2:3:4:5:6:7:8-octahydroquinoline, m.p. 142°. Isatin, (III), and KOH in H₂O at 100° afford 5-carboxy-1:2:3:4-tetrahydroacridyl-1- β -propionic acid, m.p. 307—308° (decomp.), decarboxylated at 310° to a brown oil containing a little 1:2:3:4-tetrahydroacridyl-1- β -propionic acid (V), m.p. 164—165°. *Et* 5-carboxy-1:2:3:4-tetrahydroacridyl-1- β -propionate, m.p. 174° (monohydrate, m.p. 100°), is described. (IV) is condensed with *o*-NH₂·C₆H₄·CHO

and the product is hydrolysed to (V) in 75% yield. NHPh·NH₂ and (IV) give *Et* 1:2:3:4-tetrahydrocarbazolenine-11- β -propionate (VI), b.p. 225—228°/15 mm. (methiodide, m.p. 165°), hydrolysed to 1:2:3:4-tetrahydrocarbazolenine-11- β -propionic acid, m.p. 226°. Condensation of 2-ethylcyclohexanone and NHPh·NH₂ gives 1-ethyl-1:2:3:4-tetrahydrocarbazole, b.p. 200—205°/16 mm., and 11-ethyl-1:2:3:4-tetrahydrocarbazolenine, b.p. 160—161°/16 mm. (picrate, m.p. 147°; yellow and red methiodides, m.p. 153° and 94° respectively; almost colourless ethiodide, m.p. 192°).

H. W.

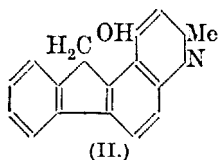
Anthraquinone group. I. 1-Amino-2-anilomethylanthraquinone. G. B. CRIPPA and R. CARRACCI (Gazzetta, 1938, 68, 820—825).—1-Amino-2-anilomethylanthraquinone, m.p. 213° (G.P. 343,064; 346,188; cf. A., 1922, i, 942), in boiling PhCHO gives 4-anilo-5-phenylantraquinono-1':2':2:3-pyrrole, m.p. 260°, also obtained from the CHPh· derivative, m.p.



321—325°, of 1-aminoanthraquinone-2-aldehyde (*loc. cit.*) and NH_2Ph at 185°.

E. W. W.

Derivatives of 2' : 3'-indeno-5 : 6-quinoline. G. K. HUGHES, F. LIONS, and L. E. A. WRIGHT (*J. Proc. Roy. Soc. New South Wales*, 1938, **71**, 449—457).—2-Aminofluorene (I) and $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in presence of a little HCl at 100° give *Et* β -2-fluorenylaminocrotonate, m.p. 96°, cyclised in paraffin oil at 280° to 4-hydroxy-2-methyl-2' : 3'-indeno-5 : 6-quinoline (II), m.p. >290°, which gives a blue fluorescence in EtOH ; the *picrate* has m.p. 231° (decomp.). Addition of (I) to $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ at 160° gives 2-acetoacetamidofluorene,



m.p. 145—146°, transformed by cold, conc. H_2SO_4 into 2-hydroxy-4-methylindeno-2' : 3'-5 : 6-quinoline, m.p. 265° (decomp.). *Et* cyclohexanone-2-carboxylate and (I) in presence of acid at 100° afford *Et* 1-2'-fluorenyl-amino- β -cyclohexene-2-carboxylate, m.p. 110°, cyclised at 290° to 5-hydroxyindeno-2' : 3'-1 : 2 : 3 : 4-tetrahydro-6 : 7-acridine, m.p. >300°. Paracetaldehyde, (I), HCl (*d* 1.19), and ZnCl_2 at 100°, followed by boiling the product with 2-5N- HCl and treatment of it with NaNO_2 , give 2-methylindeno-2' : 3'-5 : 6-quinoline, m.p. (indef.) 145—159° [methiodide, m.p. 243° (decomp.)]. Gradual addition of (I) in boiling EtOH to AcCO_2H and PhCHO in boiling EtOH yields 2-phenylindeno-2' : 3'-5 : 6-quinoline-4-carboxylic acid, m.p. 272° after darkening at 250°. Similar processes lead to 3-piperonyl-, decomp. about 245° after darkening at 220°, and 2-p-anisyl-, decomp. about 255°, -indeno-2' : 3'-5 : 6-quinoline-4-carboxylic acid. 2-Aminofluorenone (III) (dinitrophenylhydrazone, m.p. 287° after darkening at 265°) and CH_2Ac , in presence of a trace of HCl at 100° afford *Me* β -2-fluorenonylaminopropenyl ketone, m.p. 145—146°, converted by conc. H_2SO_4 at 0° into 2 : 4-dimethyl-1'-keto-2' : 3'-indeno-5 : 6-quinoline, m.p. 126°. AcCO_2H and PhCHO transform (III) into 2-phenyl-1'-ketoindeno-2' : 3'-5 : 6-quinoline-4-carboxylic acid, m.p. 205° (decomp.) after darkening at 185°, whilst 2-piperonyl-1'-ketoindeno-2' : 3'-5 : 6-quinoline-4-carboxylic acid, m.p. >290°, is derived from (III), AcCO_2H , and piperonal.

H. W.

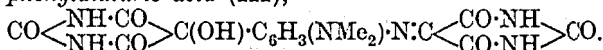
Substituted vinylbarbituric acids. II. α -Methylpropenyl derivatives. A. C. CORE and E. M. HANCOCK (*J. Amer. Chem. Soc.*, 1939, **61**, 353—354; cf. A., 1939, II, 127).— $\text{CHMe}\cdot\text{CR}\cdot\text{CALk}(\text{CO}_2\text{Et})_2$, $\text{CO}(\text{NH}_2)_2$ [or $\text{NHMe}\cdot\text{CO}\cdot\text{NH}_2$ or $\text{CS}(\text{NH}_2)_2$], and $\text{NaOEt}\cdot\text{EtOH}$ give 5-methyl-, m.p. 189.5—190.5°, 5-ethyl-, (I), m.p. 154—155°, 1-methyl-5-ethyl-, m.p. 103—104°, 5-propyl-, m.p. 157—159°, 5-allyl-, (II), m.p. 126—127°, and 5-butyl-, (III), m.p. 166—167°, -5- α -methylpropenylbarbituric acid and 5-propyl-5- α -methylpropenylthiobarbituric acid, m.p. 163—165°, which are mixtures of *cis*- and *trans*-isomerides, since with O_3 they give only traces of CH_2O (derived from the cyclic portion of the mol.) but require many recrystallisations to reach const. m.p. $\text{CN}\cdot\text{CR}(\text{CMe}\cdot\text{CHMe})\cdot\text{CO}_2\text{Et}$ gives, by way of the imine, (I) and (III) (with a little nitrile), which are sterically purer. Of these products (II) is the most effective anæsthetic.

R. S. C.

Piperazine derivatives from amino-alcohols. J. P. BAIN and C. B. POLLARD (*J. Amer. Chem. Soc.*, 1939, **61**, 532).— $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NH}_2$, $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$, and $\text{NHPh}\cdot[\text{CH}_2]_2\cdot\text{OH}$ with $\text{H}_2\text{-Cu-Cr}_2\text{O}_3$ at 250—275° give 20—50% of *trans*-2 : 5-dimethyl-, 1 : 4-di-(β -hydroxyethyl)-, m.p. 134—135°, and 1 : 4-diphenyl-piperazine, respectively.

R. S. C.

Homologues of alloxandimethylaminoanil [dimethylaminobarbiturilideneaniline] and (barbiturilideniminodimethylaminophenyl)dialuric acids. H. RUDY and K. E. CRAMER (*Ber.*, 1939, **72**, [B], 227—248; cf. A., 1938, II, 336).—If the condensation of *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{HCl}$ and alloxan (I) is effected in presence of a large excess of (I), the formation of alloxan-2-dimethylaminoanil (II) is almost entirely suppressed and two substances result, one of which, distinguished by its solubility in anhyd. $\text{C}_5\text{H}_5\text{N}$, is 5-4-dimethylamino-3'-barbiturilideniminophenylaldehydic acid (III),



(III) forms a tetrahydrate, m.p. 265—270° (decomp.) when rapidly heated in a bath preheated to 235—240°, and a monohydrate, m.p. 260—270° when rapidly heated in a bath preheated to 235—240°, either of which is converted by boiling H_2O or dil. AcOH into a sparingly sol. γ -form. The three forms are closely similar to one another, give a weakly acidic solution in H_2O , dissolve slowly in aq. NaHCO_3 , and evolve NH_3 copiously when boiled with 30% NaOH . The sol. but not the insol. form of (III) is converted by CH_2N_2 into the hygroscopic *Me*₄ derivative, m.p. 228°, insol. in dil. NaOH at room temp. (III) is transformed by Ac_2O in boiling $\text{C}_5\text{H}_5\text{N}$ into an *Ac* derivative, which melts initially at 180—230° but becomes progressively less sol. as purification proceeds and finally has m.p. >430°. (III) is obtained by the condensation of (II) and (I) in presence of HCl . CH_2N_2 in COMe_2 transforms (II) into dimethylalloxan-2-dimethylaminoanil, m.p. 186° and m.p. 250° (decomp.) after re-solidification and softening at 230°; it is insol. in cold 15% NaOH , freely sol. in cold 2N- HCl . It does not yield a *picrate*. Similarly 5 : 4'-dimethylaminophenylaldehydic acid is converted by CH_2N_2 in $\text{MeOH}\cdot\text{COMe}_2$ into 5-4-dimethylaminophenylldimethylaldehydic acid, m.p. 168—169°, transformed by Ac_2O in boiling $\text{C}_5\text{H}_5\text{N}$ into the *Ac*₁ derivative, m.p. 149—150°. 4 : 5-Dinitro-*o*-xylene is converted by NHMe_2 in EtOH at 100° into 4-nitro-5-dimethylamino-*o*-xylene, b.p. 174°/15 mm., m.p. 49—50° (*picrate*, m.p. 141—142°; *hydrochloride*, m.p. 149°), reduced ($\text{Pd}\cdot\text{CaCO}_3$ in MeOH at 40—50°) to 4-amino-5-dimethylamino-*o*-xylene (II), b.p. 133°/15 mm., m.p. 15—20° [*picrate*, m.p. 163° after softening at 153°; *hydrochloride*, m.p. 148—153° (decomp.)]; *Ac* derivative, m.p. 124°, and its *hydrochloride*]. (IV) condenses with (I) in acid medium to alloxan-5-2'-dimethylamino-4' : 5'-dimethylanil, m.p. 248° when rapidly heated or decomp. >300° when slowly heated. It reduces AgNO_3 and Fehling's solution and gives a sparingly sol. *Na* salt, and is not produced when the condensation of (IV) and (I) is attempted in EtOH in absence of acid. Also the amount of crude condensation product formed from (IV) and $\frac{1}{2}$ equivs. of (I)

Pyrimidines.—See B., 1939, 326.

Quinazolines and pyrimidines.—See B., 1939, 246.

Oxidising action of selenium dioxide. (SIGNA.) L. MONTI (R. C. Atti Accad. Lincei., 1938, [vi], 28, 96—99).—4-Hydroxy-2-methylquinazoline (I) is oxidised by SeO_2 in AcOH , at $50\text{--}60^\circ$, to 4-hydroxyquinazoline-2-aldehyde, decomp. from 210° , which with MeNO_2 in EtOH (NHMe_2) gives β -nitro- α -(4-hydroxy-2-quinazoly)ethyl alcohol, m.p. $216\text{--}218^\circ$. The prep. of (I), or of 4-hydroxyquinazoline, is improved by heating $o\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ with NH_2Ac or HCO_2NH_4 respectively in heavy petroleum at 240° for 15–20 min.

$o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in boiling N-HCl give 2-thiolmethylbenziminazole, m.p. 158° , with (?) the corresponding disulphoxide, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2$, m.p. 182° . The following benziminazoles are prepared from $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and the requisite acid: 2-phenoxyethyl-, m.p. 162° ; 2-methoxyethyl-, m.p. 136° ; 2-benzyl-, m.p. 187° ; 2- β -phenylethyl-, m.p. 186° ; 2- p -nitrobenzyl-, m.p. 215° ; 2- o -nitrobenzyl-, m.p. 217° ; 2- p -aminobenzyl-, m.p. 213° . H. W.

Heterocyclic compounds derived from 5- and 8-aminoquinoline. S. J. HAZLEWOOD, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1938, 71, 462—474).—8-Aminoquinoline (I), b.p. $174^\circ/26$ mm., $164^\circ/19$ mm., is reduced by Na and boiling abs. EtOH to 8-amino-1:2:3:4-tetrahydroquinoline (II), b.p. $145^\circ/2$ mm. (picrate, m.p. 178°), which darkens rapidly on exposure to air. It passes in boiling HCO_2H into 1:7-trimethylenebenziminazole [5:6-dihydroquinolino-1:3-diazole], m.p. 148° . With boiling Ac_2O (II) yields 2-methyl-1:7-trimethylenebenziminazole, m.p. 128° , whilst with boiling EtCO_2H and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ it affords 2-ethyl- (III), b.p. $195^\circ/20$ mm., m.p. 86° , and 2-benzyl-, m.p. 109° , 1:7-trimethylenebenziminazole. (II) and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ or (I) and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in presence of boiling 4N-HCl give 2-hydroxymethyl-1:7-trimethylenebenziminazole, m.p. 183° , whilst with $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ and $\text{dl-OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ respectively there are obtained 2- α -hydroxyethyl-, m.p. 142° , and 2- α -hydroxybenzyl-, m.p. 205° , 1:7-trimethylenebenziminazole. $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ and (I) yield 2- α -hydroxybenzhydryl-1:7-trimethylenebenziminazole, m.p. 275° . With an excess of AcCO_2H (II) affords 3-keto-2-methyl-6:7-dihydroquinolino-1:4-diazine, m.p. 113° . $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ containing dil. HCl converts (II) at room temp. into *Et* β -8-tetrahydroquinolylaminocrotonate, m.p. $56\text{--}57^\circ$, cyclised in paraffin at 280° to (III). Benzoin and (II) do not appear to react in EtOH but if fused together they yield $\text{dl-2:3-diphenyl-6:7-dihydroquinolino-1:4-diazine}$, m.p. 146° . With Ac_2 in EtOH at 0° (II) gives a compound, $\text{C}_{22}\text{H}_{26}\text{N}_4$, m.p. 123° , which appears to be an anil from 2 mols. of the base and 1 mol. of Ac_2 . Anhyd. alloxan and (II) in warm EtOH give a compound, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_4$, m.p. 255° , whereas in AcOH containing H_3BO_3 at 20° they yield a substance, (?) $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_4$, m.p. $>320^\circ$. Treatment of (I) with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and dil. HCl at 100° and heating of the product at 270° affords 4-hydroxy-2-methyl-1:10-phenanthroline, m.p. 196° after softening at 193° . Gradual addition of (I) to $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ at $140\text{--}160^\circ$ leads to 8-acetoacetamidoquinoline, m.p. 93° , which could not be cyclised by conc. H_2SO_4 . Similarly the cyclisation of *Me* β -8-quinolylaminopropionyl ketone, m.p. 95° , obtained from (I) and CH_2Ac_2 at 100° , could not be achieved by conc. H_2SO_4 , P_2O_{10} , or POCl_3 . Treatment of 5-aminoquinoline (IV) with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and dil. HCl at 100° and heating of the product to 270° yields 7-hydroxy-9-methyl-4:10-phenanthroline, m.p. $>345^\circ$. Similar treatment of (IV) with *Et* cyclohexanone-2-carboxylate appears to yield the expected acridine derivative, incipient decomposition, 250° , but an analogous product could not be obtained similarly from (I). Gradual addition of $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in CHCl_3 to (I) in CHCl_3 at 0° leads to

8-chloroacetamidoquinoline, m.p. 132° , which passes at 200° into anhydroglycolylaminoquinolinium chloride, the aq. solution of which gives an immediate ppt. of AgCl when treated with $\text{AgNO}_3\text{-HNO}_3$. H. W.

Binuclear isomerism of diphenyl type. III. G. K. HUGHES, F. LIONS, J. J. MAUNSELL, and T. WILKINSON (J. Proc. Roy. Soc. New South Wales, 1938, 71, 406—420; cf. A., 1934, 82).— γ -*o*-Carboxyphenylpentane- $\beta\delta$ -dione (I) condenses with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH to 4-*o*-carboxyphenyl-3:5-dimethylpyrazole, m.p. 250° , and with $\text{NHPh}\cdot\text{NH}_2$ to 1-phenyl-4-*o*-carboxyphenyl-3:5-dimethylpyrazole, m.p. 247° , which could not be resolved into its optical antipodes because of its weakness as an acid and its inability to form satisfactory alkaloidal salts. CH_2Ac_2 and *p*-carboxyphenylhydrazine afford 1-*p*-carboxyphenyl-3:5-dimethylpyrazole, m.p. 158° , whilst (I) similarly gives 1-*p*-carboxyphenyl-4-*o*-carboxyphenyl-3:5-dimethylpyrazole, m.p. 133° ; this gives a strychnine salt, m.p. 187° , which has not been completely examined. *p*-Carbethoxyphenylhydrazine is converted by CH_2Ac_2 into 1-*p*-carbethoxyphenyl-3:5-dimethylpyrazole, m.p. 65° , and by (I) into 4-*o*-carboxyphenyl-1-*p*-carbethoxyphenyl-3:5-dimethylpyrazole, m.p. 139° . With $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, (I) yields 4-*o*-carboxyphenyl-3:5-dimethylpyrazole-1-carboxylamide, m.p. 189° . Homophthalic acid and 1-*o*-aminophenylpiperidine (II) at 180° afford 1:3-diketo-2-*o*-piperidinophenyl-1:2:3:4-tetrahydroisquinoline, m.p. 143° (*CHPh* derivative, m.p. $160\text{--}161^\circ$), which does not appear to give quaternary NH_4 salts. 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ and (II) at 100° yield 2:4-dinitro-2'-piperidinodiphenylamine, m.p. 174° , reduced ($\text{SnCl}_2\text{-HCl-Sn}$ in boiling EtOH) to 2:4-diamino-2'-piperidinodiphenylamine, m.p. 157° . *Et* phenacylacetoacetate (III) is converted by 4-aminoveratrole in boiling EtOH containing AcOH into *Et* 5-phenyl-1-3':4'-dimethoxyphenyl-2-methylpyrrole-3-carboxylate, m.p. 115° , by *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ into *Et* 5-phenyl-1-*o*-carboxyphenyl-2-methylpyrrole-3-carboxylate, m.p. 110° , and by *o*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$ into *Et* 5-phenyl-1-*o*-xenyl-2-methylpyrrole-3-carboxylate, m.p. $150\text{--}151^\circ$. $(\text{CH}_2\text{Ac})_2$ and (II) afford 1-*o*-piperidinophenyl-2:5-dimethylpyrrole, m.p. 72° , which does not appear to form a methiodide or a methosulphate. With phenacyl-lævulic acid (II) yields 2-phenyl-1-*o*-piperidinophenylpyrrole-5- β -propionic acid, m.p. 151° , the acidic properties of which are not sufficiently pronounced to enable it to form alkaloidal salts. (II) and (III) give *Et* 5-phenyl-1-*o*-piperidinophenyl-2-methylpyrrole-3-carboxylate, m.p. $102\text{--}103^\circ$. $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and (II) in boiling AcOH afford *o*-piperidinophenylphthalimide, m.p. $119\text{--}120^\circ$, which does not appear to form a methiodide or a methosulphate. (II) is acetylated and converted by MeI into 1-*o*-acetamidophenylpiperidine methiodide, m.p. $217\text{--}218^\circ$. Successive additions of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and $\text{CH}_2\text{Cl}\cdot\text{COEt}$ to Na in Et₂O lead to *Et* α -acetyl- β -propionylpropionate, b.p. $146^\circ/26$ mm., $251^\circ/760$ mm., converted by K_2CO_3 in boiling H_2O into heptane- $\beta\delta$ -dione (IV), b.p. $90^\circ/21$ mm., about $194^\circ/760$ mm. (semicarbazone, m.p. 231°), which is transformed by $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ in boiling EtOH containing AcOH into 1- β -naphthyl-2-methyl-5-ethylpyrrole, m.p. 102° . H. W.

Naphthiminazoles.—See B., 1939, 256.

m- and *p*-Bis-(5'-keto-2' : 3'-dimethyl-1'-pyrazolyl)benzene (" *m*- and *p*-diantipyrine "). J. BÖSEKEN and J. B. ROOS (Rec. trav. chim., 1939, 58, 58—62).—The *m*-phenylenedihydrazone of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ (A., 1933, 1285; cf. also A., 1934, 67) and the corresponding *p*-compound with AcOH in boiling xylene give *m*-, m.p. 185—187°, and *p*-bis-(5'-keto-3'-methyl-1'-pyrazolyl)benzene, which with $\text{MeI}\cdot\text{MeOH}$ at 110° give *m*-, m.p. 177—179°, and *p*-bis-(5'-keto-2' : 3'-dimethyl-1'-pyrazolyl)benzene, m.p. 300°, respectively (" *m*- and *p*-diantipyrine ").

E. W. W.

Salts of 6 : 8-diamino-2-hydroxypurine. J. R. SPIES and T. H. HARRIS, jun. (J. Amer. Chem. Soc., 1939, 61, 351—352).—Addition of 2 : 4-

$\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{N}_2\text{Cl}$ to 6-amino-2-hydroxypurine sulphate in NaOH at 0—10° gives the diazo-compound, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to 6 : 8-diamino-2-hydroxypurine [sulphate, $+3\text{H}_2\text{O}$ ($1\text{H}_2\text{O}$ retained at 139°/vac.); hydrochloride, anhyd. and $+1.5\text{H}_2\text{O}$; acetate, anhyd. and $+3.5\text{H}_2\text{O}$; carbonate, anhyd. and $+2\text{H}_2\text{O}$; picrate, anhyd. and $+0.5\text{H}_2\text{O}$].

R. S. C.

Phthalocyanines.—See B., 1939, 249.

Porphyryns. XLIII. Chemistry of pyrrole.

H. FISCHER and E. ELHARDT (Z. physiol. Chem., 1939, 257, 61—105; cf. A., 1937, II, 168, 169).—Attempts to synthesise pyrrole-3-acetic-5-propionic acid with a view to the synthesis of uroporphyrin I and octachloroporphin as a means of improving the synthesis of porphyrin are described. 5-Carbethoxy-2-methyl-4-cyanomethylpyrrole (I) in Et_2O gives, with 4.5 mols. of SO_2Cl_2 , *Et* 3-chloro-2-trichloromethyl-4-cyanomethylpyrrole-5-carboxylate, m.p. 211—212° (decomp.), which yields a substance, m.p. 128° (possibly *Et*₂ 3-chloro-4-cyanomethylpyrrole-2 : 5-dicarboxylate), when boiled with aq. EtOH . With 4 mols. of SO_2Cl_2 (I) in Et_2O gives a product which, when boiled with H_2O for 48 hr., yields a substance, $\text{C}_8\text{H}_6\text{O}_4\text{N}_2$, m.p. 234° (probably 4-cyanomethylpyrrole-2 : 5-dicarboxylic acid). *Me* 2-methylpyrrole-4-acetate in EtOH with HCN and HCl gas gives an iminochloride, decomposed by NH_3 to *Me* 5-aldehydo-2-methylpyrrole-4-acetate, m.p. 181—182° (oxime, m.p. 217°), which condenses with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in presence of NH_2Me , HCl and Na_2CO_3 to the substance, $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_2$, m.p. 142°. 5-Aldehydo-2 : 4-dimethylpyrrole with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in presence of NH_2Ph gives 2 : 4-dimethyl-5- ω -cyano- ω -carbethoxyvinylpyrrole, m.p. 126—129°, which in CHCl_3 with excess of HCN gives the corresponding 3-aldehydo-compound, m.p. 184° converted into 3 : 5-dialdehydo-2 : 4-dimethylpyrrole, m.p. 165°, by conc. aq. KOH . 2-Carboxy-5-carbethoxy-4-methylpyrrole-3-propionic acid in $\text{Et}_2\text{O}\cdot\text{MeOH}$ gives, with CH_3N_3 , *Me* 2-carbomethoxy-5-carbethoxy-4-methylpyrrole-3-propionate, m.p. 66—68°. This substance, in Et_2O , yields with SO_2Cl_2 a compound which, when boiled with H_2O , gives a Cl-free substance, m.p. 136°. 5-Carbethoxy-2-methylpyrrole in Et_2O treated twice with 3 mols. of SO_2Cl_2 affords *Et* 3 : 4-dichloro-2-chloromethylpyrrole-5-carboxylate (II), m.p. 160—161° (brown colour) (*OMe*-, m.p. 115°, *OEt*-, m.p. 105°, and *NHPh*-, m.p. 145°, derivatives), which, boiled with H_2O , gives H_2O -insol. 3 : 3' : 4 : 4'-

tetrachloro-5 : 5'-dicarbethoxypyrromethane (III), m.p. 210—211° (yield almost quant. if H_2O vol. small and duration of boiling brief) (free dicarboxylic acid, darkens 205°, m.p. $<350^\circ$), and the H_2O -sol. compound (IV), m.p. 145°, resulting from replacement of CH_2Cl by $\text{CH}_2\cdot\text{OH}$. (III) is also obtained together with the formate, m.p. 168°, of (IV) by boiling (II) with HCO_2H . 5-Carbethoxy-2-methylpyrrole in Et_2O with >4 mols. of SO_2Cl_2 gives *Et* 3 : 4-dichloro-2-dichloromethylpyrrole-5-carboxylate (XI), m.p. 94°; with ~ 6 mols. of SO_2Cl_2 it gives the chloride (V), m.p. 142—144°, of *Et* 3 : 5-dichloro-2-carboxypyrrole-5-carboxylate (VI), m.p. 275° (decomp.; darkens). With boiling aq. EtOH (V) gives *Et* 3 : 4-dichloropyrrole-2 : 5-dicarboxylate (X), m.p. 116°, hydrolysed to the acid, decomp. 260—300° [corresponding anilide, m.p. 174°, hydrazide (VII), m.p. 224°, amide (VIII), m.p. 270°, hydroxamic acid, decomp. 191°]; with 2 mols. of MgMeI the corresponding tert. alcohol, m.p. 107—108°; in C_6H_6 with Na (VI) and 3 : 3' : 4 : 4'-tetrachloro-5 : 5'-dicarbethoxydipyrrolyl diketone, m.p. 219—220°, and with NaN_3 a good yield of the corresponding azide (IX), m.p. 143° (explodes), also obtained in poor yield from (VII) in 50% aq. AcOH at 0° with NaNO_2 . (VI) at 290° gives *Et* 3 : 4-dichloropyrrole-5-carboxylate, m.p. 110—112°. (VIII) boiled for 45 min. with NaOAc and Ac_2O gives the substance, (?) $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_2\text{Cl}_2$, m.p. 123°, and (IX) boiled with MeOH for 1 hr. gives the corresponding methylurethane, m.p. 174—176°. (X) boiled for 5 min. with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ gives the corresponding dihydrazide, colours 280°, decomp. 312°, which with COMe_2 gives the compound, $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_5\text{Cl}_2$, m.p. 276° (decomp.), and, in 80% aq. AcOH with NaNO_2 at -7° to -2° the corresponding diazide, explodes 144°. (II) in AcOH with CrO_3 in H_2O at 60° gives *Et* 3 : 4-dichloro-2-aldehydopyrrole-5-carboxylate, m.p. 150° (oxime, m.p. 185°) [also obtained in better yield from (XI) and boiling 50% aq. EtOH], hydrolysed to the acid, m.p. 240° (decomp.), also obtained by boiling (XI) with EtOH , adding aq. NaOH , and again boiling. *Et*₂ 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate (XII) in EtOH gives, with 2 mols. of SO_2Cl_2 , 2 : 5-di(chloromethyl)-, m.p. 158°, and with 4 mols. of SO_2Cl_2 , *Et* 2 : 5-di(dichloromethyl)-pyrrole-3 : 5-dicarboxylate, m.p. 117—119°, which, boiled for 6 hr. with H_2O with frequent addition of a few drops of aq. Na_2CO_3 , gives a substance, m.p. 255°, possibly *Et*₂ 2 : 5-dialdehydopyrrole-3 : 4-dicarboxylate (diphenylhydrazone, m.p. 160—162°), and boiled for 2 days with 50% aq. EtOH gives a substance, m.p. 218°, of high N content. (XII) in Et_2O with 8 mols. of SO_2Cl_2 gives a substance, $\text{C}_{12}\text{H}_{12}\text{O}_4\text{NCl}_5$, m.p. 127°, with 10 mols. of SO_2Cl_2 followed by boiling for 2 days with EtOH a substance, m.p. 79° (possibly *Et*₂ 2 : 5-di(trichloromethyl)pyrrole-3 : 4-dicarboxylate), and with 4 Br a Br-compound (probably a perbromide) which reacts with EtOH and with COMe_2 to give a substance, $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}$, m.p. 239—241°, probably 3-carboxy-4-carbethoxy-2 : 5-dimethylpyrrole. The Br-compound with NH_2Ph gives (XII). *Et* 3-cyano-2 : 4-dimethylpyrrole-5-carboxylate boiled with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ gives the corresponding hydrazide, m.p. 268°, converted, in 80% aq. AcOH , by NaNO_2 into the corresponding azide, decomp. 138°, which yields the corresponding methyl-

urethane, m.p. 192°, when boiled with MeOH. Similarly Et 2:3:4-trimethylpyrrole-5-carboxylate gives the corresponding *hydrazide*, m.p. 236°, and *azide*, decomp. 145°. This *azide*, boiled with MeOH for 2 days, yields a *substance*, $C_8H_{14}O_2N_2$, decomp. 187°; treated in Et₂O with 1 mol. of SO₂Cl₂ it yields the unstable light-sensitive *azide*, becomes red-brown at 130°, decomp. 141°, of 3:4-dimethyl-2-chloromethylpyrrole-5-carboxylic acid and treated with 2 mols. of SO₂Cl₂ it yields the unstable, light-sensitive *azide* (XIII), decomp. 129°, of 3:4-dimethyl-2-dichloromethylpyrrole-5-carboxylic acid. (XIII) boiled for 2 hr. with aq. EtOH gives the *hydrochloride*, decomp. slowly >250°, of the 5:5'-diethylurethane of 3:3':4:4'-tetramethylpyrromethene. The oxime of Et 5-aldehydo-2-methylpyrrole-3-carboxylate, boiled with NaOAc and Ac₂O for 30 min., gives Et 5-cyano-2-methylpyrrole-3-carboxylate, m.p. 129°, but the attempt to introduce a 4-CHO into this compound fails. Et 3-aldehydo-2-methylpyrrole-5-carboxylate in AcOH gives with Br the corresponding 4-Br-derivative, m.p. 188° (excess of Br does not attack Me), and with NH₂OH the 3-oxime, m.p. 197°, which is converted by NaOAc and Ac₂O into the corresponding 3-CN-compound (XIV), m.p. 125°, a *substance*, m.p. 306° (decomp.), being produced simultaneously. (XIV) is hydrolysed to 3-cyano-2-methylpyrrole-5-carboxylic acid, m.p. 273° (decomp.), by aq. NaOH, and in AcOH with Br it gives Et 4-bromo-3-cyano-2-methylpyrrole-5-carboxylate, m.p. 196°, the Br of which does not react with NH₂Ph. With 2—4.5 mols. of SO₂Cl₂ under various conditions (XIV) yields Et 4-chloro-3-cyano-2-methylpyrrole-5-carboxylate, m.p. 191°, and Et 4-chloro-3-cyano-2-chloromethylpyrrole-5-carboxylate, m.p. 138—140° (boiled for 1 hr. with H₂O this yields the corresponding 2-OH·CH₂ compound, m.p. 180°). When treatment with SO₂Cl₂ is followed by boiling for 2 hr. with 50% aq. MeOH 2-Me 5-Et 4-chloro-3-cyanopyrrole-2:5-dicarboxylate, m.p. 187°, and when it is followed by boiling for 2 hr. with aq. EtOH Et₂ 4-chloro-3-cyanopyrrole-2:5-dicarboxylate (XV), m.p. 166°, are obtained, a Cl-compound, m.p. 114°, being also produced in the second case. If this compound is boiled with H₂O Et 4-chloro-3-cyano-2-carboxypyrrole-5-carboxylate, m.p. (rapid heating) 252—254° (slow heating, decomp. 245—248°), is obtained. (XV) in conc. aq. NH₃ at 130° for 10 hr. gives 4-chloro-3-cyano-2:5-dicarbamylpyrrole, m.p. 344° (decomp.; blackens 335°). Et 3-aldehydo-2-methyl-4-ethylpyrrole-5-carboxylate yields the *oxime*, m.p. 167°, which gives the corresponding 3-CN-compound, m.p. 138°. This in Et₂O with SO₂Cl₂ gives Et 2-dichloromethyl-3-cyano-4-ethylpyrrole-5-carboxylate, m.p. 110°; when treatment with SO₂Cl₂ is followed by boiling with H₂O the 2-OH·CH₂, m.p. 128° and the 2-CHO, m.p. 148°, derivatives of Et 3-cyano-4-ethylpyrrole-5-carboxylate are obtained. Et 3-cyano-2:4-dimethylpyrrole-5-carboxylate in Et₂O boiled for several hr. with SO₂Cl₂ gives Et 3-cyano-4-methyl-2-dichloromethylpyrrole-5-carboxylate, m.p. 123°, converted into Et 2-aldehydo-3-cyano-4-methylpyrrole-5-carboxylate, m.p. 158° (*oxime*, m.p. 198°, obtained in the cold; when heat is used, a *substance*, m.p. 259°, is also obtained), by boiling with 50% aq. EtOH. The oxime is con-

verted in the usual way into Et 2:3-dicyano-4-methylpyrrole-5-carboxylate, m.p. 135°. The effects of substituents on the acidity of derivatives of pyrrole have been determined by titration and it is shown that some of the derivatives act as acids although containing no true acid group. 4-Cl and 4-Br confer acidity.

W. McC.

Protochlorophyll and vinylphæoporphyrin-a₅. H. FISCHER, H. MITTENZWEI, and A. OESTREICHER (Z. physiol. Chem., 1939, 257, IV—VII; cf. A. 1936, 1393; Noack and Kiessling, A., 1931, 247).—Methylphæophorbide-a (I) in HCO₂H boiled for 3–5 min. with Fe powder yields a complex Fe salt, converted by 20% HCl or, better, by leaving overnight in Et₂O, followed by treatment with CH₂N₂, into vinylphæoporphyrin-a₅ (II), m.p. >320°, which gives a *cryst. compound* when heated for 12 hr. at 100° with CHN₂·CO₂Et followed by treatment with CH₂N₂ and is identical with the product obtained from protochlorophyll by removal of Mg with H₂C₂O₄. The chief component of the chlorophyll of the skins of gourd seeds is the Mg salt of (II). (II) is also obtained from 10-acetoxyvinylphæoporphyrin-a₅ by hydrolysis with conc. H₂SO₄ (which gives 10-hydroxyvinylphæoporphyrin-a₅) followed by long treatment with HCO₂H at 50–60°. When the treatment given to (I) is applied to pyrophæophorbide-a, vinylphyloerythrin, m.p. >33°, spectroscopically identical with (II), is obtained. (II) with dil. KOH in MeOH gives vinylchloroporphyrin-e₆, reconverted into (II) by C₅H₅N and Na₂CO₃.

W. McC.

Bile pigments. XXI. Aminohydroxypyrromethenes. Pentduopent reaction. H. FISCHER, H. REINECKE, and H. LICHTENWALD (Z. physiol. Chem., 1939, 257, 190—200; cf. A., 1935, 994; 1938, II, 509).—The azo-dye from the Me ester of neoxanthobilirubinic acid gives, with hot AcOH and Zn powder, Me 5'-amino-5-hydroxy-3':4'-dimethyl-3-ethylpyrromethene-4'-propionate, m.p. 202° (Ac₁ derivative, m.p. 216°). In the same way the azo-dye from the Me ester of isoneoxanthobilirubinic acid (I) gives Me 5'-amino-5-hydroxy-3':3'-dimethyl-4-ethylpyrromethene-4'-propionate, m.p. 181° (Ac₁ derivative, m.p. 216°), also obtained from the azo-dye of the Me ester of (I) by catalytic reduction (PtO₂—H₂—AcOH); that from the Me ester of isocoproneoxanthobilirubinic acid gives Me₂ 5'-amino-5-hydroxy-3':3'-dimethylpyrromethene-4:4'-dipropionate, m.p. 171°, and that from the Me ester of coproneoxanthobilirubinic acid (II) gives Me₂ 5'-amino-5-hydroxy-4:3'-dimethylpyrromethene-3:4'-dipropionate, m.p. 180° (Ac₁ derivative, m.p. 185°). The no. of H in the Ac derivatives is 2 < the calc. no. but catalytic reduction does not introduce 2 H. The aminohydroxypyrromethenes when warmed with strong alkali or treated successively with NaNO₂ and NaOH give the pentduopent reaction. If the solution is diluted the reaction is negative but becomes positive after warming with Na₂S₂O₄. Opsopyrrole (III) in MeOH couples with PhN₂Cl to give a bisazo-dye (IV), m.p. 222° [dihydrochloride, m.p. 185°; complex Cu salt, C₂₆H₂₆N₆Cu, m.p. 234° (decomp.), 2 pyrrole rings to 1 Cu, stable to alkali, acid eliminates Cu], and with diazotised p-C₆H₄Me·NH₂ the corresponding bisazo-dye. On catalytic hydrogenation

(IV) takes up first 8 H and then, after separation of the rings, 2 H. The carboxylic acid of (III) in CHCl_3 with MeOH and PhN_2Cl followed by treatment with HBr gives the *hydrobromide*, m.p. 203° , of the azo-dye (V), $\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_6$, and in the same way the aldehyde of the carboxylic acid gives the azo-dye (VI), $\text{C}_{15}\text{H}_{15}\text{O}_3\text{N}_3$, m.p. 145° (*oxime*, m.p. 158°). The carboxylic acid of (III) treated with H_2O_2 in $\text{C}_5\text{H}_5\text{N}$ gives 5-hydroxy-3-methylpyrrole-4-propionic acid (VII), m.p. 187° , and a substance, $\text{C}_8\text{H}_{11}\text{O}_3\text{N}$, m.p. 169° (cf. A., 1937, II, 215). (VI) and the carboxylic acid boiled for 8 hr. in MeOH containing HBr followed by treatment with conc. HCl give the hydrochloride of Me_2 5-hydroxy-5'-azobenzene-4 : 3'-dimethylpyrromethene-3 : 4'-dipropionate and, similarly, (VI) and (VII) give the hydrochloride of Me_2 5-hydroxy-5'-azobenzene-3 : 3'-dimethylpyrromethene-4 : 4'-dipropionate. W. McC.

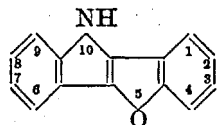
Adsorption values of porphyrins.—See A., 1939, I, 195.

[Tautomerism of oximes.] A. H. BLATT (J. Org. Chem., 1938, 3, 506—507; cf. A., 1939, II, 38).—Many corrections of formulæ are made. H. W.

Benzoylformyloxindolephenylhydrazones.—
See A., 1939, I, 178.

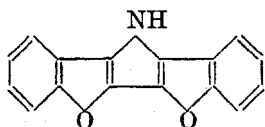
Oxazines.—See B., 1939, 297.

Indoles. V. Coumarono(3, 2-b)indole and derivatives. J. W. CORNFORTH, G. K. HUGHES, F. LIONS, and R. H. HARRADENCE (J. Proc. Roy. Sci. New South Wales, 1938, **71**, 486—493).—Coumaranone (I) and $\text{NHPh}\cdot\text{NH}_2$ at 100° give a gummy phenylhydrazone, which passes in boiling glacial AcOH into *coumarono*-(3, 2-b)-*indole* (II), m.p. 198° . The 7-methyl-, m.p. 183° , 7-bromo-, m.p. 159° , 6:7-benz-, m.p. 166° , and 10-methyl-, m.p. 240° , -derivatives are obtained analogously from (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}_2$,

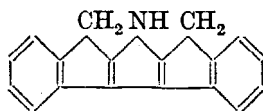


(II.)

p -C₅H₄Br·NH·NH₂, β -C₁₀H₇·NH·NH₂, and NPhMe·NH₂, respectively. (I), N₂H₄·H₂SO₄, and NaOAc in boiling EtOH-H₂O yield *coumaranoneazine* (III), m.p. 207–208°, which is not hydrolysed by HCl-MeOH but is readily affected by aq. HCl. Boiling glacial AcOH transforms (III) into *dicoumaronopyrrole* (IV), m.p. 330°. 2-*Hydrindoneazine*, m.p. 195–196°, is very readily cyclised to 2:1:2':1'-*di-indeno-2:3:4:5-pyrrole* (V), m.p. >360°, by treatment with cold, 5% HCl-MeOH or HCl-EtOH, by passing dry HCl into its suspension in Et₂O, or by boiling it for a few min. with glacial



(IV.)



(V.)

AcOH, whereas 3-hydrindoneazine affords only 1:2:1':2'-di-indeno-2:3:4:5-pyrrole, m.p. $>360^{\circ}$, when dry HCl is passed over the fused material at about 170° . H. W.

Cyanine dyes.—See B., 1939, 328.

Thi- and selen-azoles.—See B., 1939, 245, 248.

Rhodanine dyes [photosensitisers].—See B., 1939, 328.

Cactus alkaloids. XX. *O*-Methyl-*d*-anhalonidine. E. SPÄTH and J. BRUCK (Ber., 1939, 72, [B], 334—338; cf. A., 1938, II, 71).—Repeated fractional extraction of the mother-liquors from the non-phenolic bases of mezcal buttons gives portions from which, after treatment with tartaric acid in MeOH, *N*-methylmescaline and *d*-*O*-methylanhalonidine (I) [d-6 : 7 : 8-trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline], b.p. 140° (bath)/0.05 mm., $[\alpha]_D^{25} + 20.7^\circ$ in MeOH [2 : 4 : 6-trinitrobenzoyl derivative (II), m.p. 259—260° (vac.), $[\alpha]_D^{25} + 39.7^\circ$ in CHCl_3], are isolated. The constitution of (I) follows from the identity of (I) and (II) with the compounds obtained by the resolution of synthetic *r*-6 : 7 : 8-trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline with *d*-tartaric acid in H_2O . The *l*-base has $[\alpha]_D^{25} - 20.1^\circ$ in MeOH [2 : 4 : 6-trinitrobenzoyl derivative, m.p. 259—260° (vac.), $[\alpha]_D^{25} - 43.7^\circ$ in CHCl_3]. H. W.

Carnosine and anserine. V. DU VIGNEAUD and O. BEHRENS (Ergebn. Physiol., 1939, 41, 917—973).—A review.

Cinchona alkaloids. XXX. Syntheses in the series of the cinchona alkaloids. P. RABE and K. KINDLER (Ber., 1939, **72**, [B], 263—264).—*epi*Quinine *epiquinidine* sulphate, $C_{20}H_{24}O_2N_2 \cdot C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot 6H_2O$, has been isolated from the residue left after removal of quinine and quinidine from the products of the reduction of quinone by Al powder and NaOEt in EtOH (cf. A., 1918, I, 303). Normal *epiquinine hydrobromide*, m.p. 71—77°, decomp. 108°, and normal *epiquinidine thiocyanate*, m.p. 193°, are described. H. W.

Modified cinchona alkaloids. VI. Niquidine.
E. M. GIBBS and T. A. HENRY (J.C.S., 1939, 240—246).—Quinidine with HI-P gives α -iododihydroquinidine, m.p. 202° (decomp.), $[\alpha]_D^{25} + 259^\circ$ in 0.1N-HCl [*dihydrochloride* (+5.5H₂O), m.p. 202° (decomp.), $[\alpha]_D^{25} + 224.4^\circ$ in 0.1N-HCl; *acid sulphate* (+4H₂O), m.p. 172° (decomp.), $[\alpha]_D^{25} + 212.3^\circ$ in 0.1N-HCl], and with HBr affords a mixture of α -, decomp. 235°, $[\alpha]_D^{25} + 271.2^\circ$ in 0.1N-HCl [*acid sulphate* (+4H₂O), m.p. 180°, $[\alpha]_D^{25} + 217.2^\circ$ in 0.1N-HCl], and α' -*bromodihydroquinidine* (+3H₂O), m.p. 210° (decomp.), $[\alpha]_D^{25} + 231.7^\circ$ in 0.1N-HCl [*nitrate*, m.p. 225° (decomp.); *dihydrobromide* (+3H₂O), m.p. 235° (decomp.), $[\alpha]_D^{25} + 166^\circ$ in H₂O; *sulphate* (+3H₂O), m.p. 207°, $[\alpha]_D^{25} + 206.1^\circ$ in 0.1N-HCl]. Debromination of crude bromodihydroquinidine with AgNO₃ gives CH₂O and “niquidine” (cf. Domanski and Suszko, A., 1936, 490), which can be separated into *niquidine* (I), probably

$$\text{CHMe} \cdot \text{CH} \cdot \text{CH} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \end{array} \text{CH} \cdot \text{CH} \cdot \text{Q} \cdot \text{OH} \quad (\text{Q} = \text{quinolyl or 6-methoxyquinolyl}), \text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2, \text{ m.p. } 172^\circ, [\alpha]_D^{25} + 301.5^\circ \text{ in } 0.1\text{N-H}_2\text{SO}_4 \text{ [dihydrobromide (+2H}_2\text{O), m.p. } 230^\circ \text{ (decomp.), } [\alpha]_D^{25} + 198.7^\circ \text{ in H}_2\text{O}], \text{ and isoquinidine (II), C}_{19}\text{H}_{24}\text{O}_2\text{N}_2, \text{ m.p. } 163^\circ, [\alpha]_D^{25} + 222.0^\circ \text{ in } 0.1\text{N-H}_2\text{SO}_4. \text{ Hydrogenation (H}_2\text{-PtO}_2\text{) of either (I) or (II) yields dihydroniquidine, m.p. } 165^\circ, [\alpha]_D^{25} + 231.6^\circ \text{ in } 0.1\text{N-H}_2\text{SO}_4 \text{ [sulphate (+2H}_2\text{O), m.p. } 180^\circ, [\alpha]_D^{25} + 200.4^\circ \text{ in } 0.1\text{N-H}_2\text{SO}_4; \text{ NO-derivative,}$$

m.p. 170°; *N*-Me derivative, m.p. 212°, $[\alpha]_D^{25} +234^\circ$ in 0.1N- H_2SO_4 ; *phenylthiocarbamide*, m.p. 112°, indicating that (I) and (II) are geometrical isomerides. The H_2 -base in AcOH is converted by boiling into *epi*- C_9 -dihydroniquidine, $[\alpha]_D^{25} -140.8^\circ$ in 0.1N- H_2SO_4 [*sesquihydrobromide* ($+H_2O$), m.p. 240° (decomp.), $[\alpha]_D^{25} -102.8^\circ$ in 0.1N- H_2SO_4 ; *sesquinitrate* ($+2H_2O$), m.p. 196° (decomp.), $[\alpha]_D^{25} -110.3^\circ$ in 0.1N- H_2SO_4], also obtained from *epi*- C_9 -quinidine through *iododihydroepi*- C_9 -quinidine, m.p. 150—155° (decomp.).

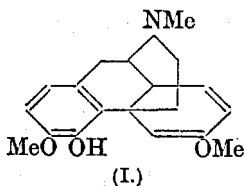
F. R. S.

Addition of Grignard's reagent to ψ -codeine types. III. *Methylidihydrothebaines*. L. SMALL and E. M. FRY (J. Org. Chem., 1939, 3, 509—540; cf. A., 1936, 490, 1277).—Gradual addition of thebaine to a solution of MgMeI in boiling Et_2O gives mainly α -methylidihydrothebaine (I), m.p. 87.5—89.5°, $[\alpha]_D^{25} +140^\circ$ in EtOH (*perchlorate*, $[\alpha]_D^{25} +84^\circ$ in EtOH; *methiodide*, m.p. 219—221°, $[\alpha]_D^{25} +76^\circ$ in EtOH), which could not be hydrogenated (Adams) catalyst in EtOH or PtO_2 - PdO_2 and is not affected by short boiling with conc. HCl. The *acetate* (*perchlorate*, $[\alpha]_D^{25} +78^\circ$ in EtOH, and *methiodide hemihydrate*, m.p. 193—195°, $[\alpha]_D^{25} +55^\circ$ in EtOH) is described. MeI and NaOH convert (I) into α -methylidihydrothebaine *Me ether methiodide*, m.p. 177—178°, $[\alpha]_D^{25} +43.3^\circ$ in EtOH, with an unidentified by-product, m.p. about 60° and $>230^\circ$ after resolidification at about 100°, $[\alpha]_D^{25} \pm 0^\circ$. Boiling 40% NaOH transforms (I) into α -methylidihydrothebaineisomethine (II) (*Na salt*), isolated as the *salicylate* (III), m.p. 163—164.5°, $[\alpha]_D^{25} -90^\circ$ in EtOH, and *methiodide* (IV), m.p. 227—230°, $[\alpha]_D^{25} -80^\circ$ in EtOH. Reduction (Adams) of (II) affords non-cryst. *dihydro*- α -methylidihydrothebaineisomethine, isolated as the *salicylate*, m.p. 165—167°, $[\alpha]_D^{25} -47.7^\circ$ in EtOH. (IV) is extremely resistant to the ordinary Hofmann degradation but is converted by TIOH followed by boiling 50% NaOH into the optically inactive, non-cryst. *vinylidihydro*- α -methylthebaol (V) (*Na salt*); the corresponding *Ac derivative*, m.p. 103—105.5°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH, absorbs 2 H_2 forming a non-cryst. substance hydrolysed to a non-cryst. compound. Successive treatment of (II) with boiling conc. HCl, NH_3 , MeI, and 40% NaOH gives a mixture of (+)-6-methoxy- α -methylthebentriene (VI), m.p. 99—101°, $[\alpha]_D^{25} +9^\circ$ in EtOH, and *r*-6-methoxy- α -methylthebentriene, m.p. 91.5—93.5°, obtained also by admixture of equal amounts of the corresponding optical antipodes and by the action of boiling, conc. HCl on (V). (VI) is not racemised or hydrolysed by conc. HCl but is reduced (PtO_2 in EtOH) to 6-methoxy- α -methylthebendiene, m.p. 56—59.5°, $[\alpha]_D^{25} -5^\circ$ in EtOH. Boiling AcCl transforms (III) into an alkali-sol., non-cryst. base (*salicylate*; *benzoate*; *phthalate*, m.p. 150—160°; *fumarate*; *picrate*, m.p. 172—180°) and an alkali-insol. α -9-dimethylamino-6-methoxy- α -methylthebendiene, m.p. 76.5—78°, $[\alpha]_D^{25} -82^\circ$ in EtOH, which is indifferent towards catalytic hydrogenation; the corresponding *methiodide*, m.p. 115—117°, $[\alpha]_D^{25} -51^\circ$ in EtOH, is degraded (Hofmann) to (VI). Passage of (I) over Zn dust-pumice at a dull red heat gives a small proportion of phenanthrene, also obtained at a lower temp. with an unidentified compound, m.p. 116—120° (*picrate*, 133—134°). Non-

cryst. δ -methylidihydrothebaine (VII) [*perchlorate*, $[\alpha]_D^{25} +50^\circ$ in EtOH; non-cryst. *Ac derivative* (*perchlorate*, $[\alpha]_D^{25} +67.5^\circ$ in EtOH; *methiodide* ($+H_2O$), softens at 109° and m.p. 198° after becoming dehydrated, $[\alpha]_D^{25} +56^\circ$ in EtOH)] is obtained as a by-product of the prep. of (I) or by treating the *perchlorate* of (I) with boiling EtOH. The base and its hydrochloride are not hydrogenated (Adams) in EtOH. Treatment of the amorphous *methiodide* of (VII) with boiling 40% NaOH yields the non-cryst. δ -methylidihydrothebaineisomethine (VIII) (*salicylate*, m.p. 209—211° after softening slightly at 190°, $[\alpha]_D^{25} -16^\circ$ in EtOH; *methiodide monohydrate*, m.p. 176.5—178.5° and 233° after resolidification at 180°, $[\alpha]_D^{25} -30^\circ$ in EtOH). δ -Methylidihydrothebaineisomethine *Me ether methiodide*, m.p. 172.5—174°, $[\alpha]_D^{25} -25^\circ$ in EtOH, is converted by the successive action of 40% NaOH and picric acid into δ -methylidihydrothebaineisomethine *Me ether picrate*, m.p. 172—174°. Hydrogenation (PtO_2 in EtOH) of (VIII) gives the non-cryst., phenolic *dihydro*- δ -methylidihydrothebaineisomethine [*salicylate* (IX), m.p. 182.5—185.5°, $[\alpha]_D^{25} +12.8^\circ$ in EtOH], the *methiodide* of which is degraded to (V). AcCl, pretreated with a little H_2O , transforms (VIII) into a compound hydrolysed by NaOH to *hydroxydihydro*- δ -methylidihydrothebaineisomethine, m.p. 163—165°, $[\alpha]_D^{25} +25^\circ$ in EtOH, transformed by AcCl-HCl into δ -9-dimethylamino-6-methoxy- α -methylthebendiene, m.p. 101.5—103°, $[\alpha]_D^{25} +33^\circ$ in EtOH, which is indifferent towards catalytic hydrogenation. The closure of the thebanene ring is accomplished in a single operation when (IX) is boiled with AcCl. Degradation of δ -9-dimethylamino-6-methoxy- α -methylthebendiene *methiodide* ($+0.5H_2O$), softens at 155°, m.p. 207—208°, $[\alpha]_D^{25} -13^\circ$ in EtOH, occurs only slowly in boiling 40% NaOH but with more conc. alkali it proceeds smoothly, giving (VI) in 86% yield. When heated at 98°/vac. acetyl- δ -methylidihydrothebaine methohydroxide passes into (—)-methylidihydrothebaineisomethine (X), m.p. 106—108°, $[\alpha]_D^{25} -21.3^\circ$ in EtOH (*tartrate*, m.p. 135—140°, $[\alpha]_D^{25} -7^\circ$ in EtOH; corresponding *Me ether methiodide*, m.p. 190—192°, $[\alpha]_D^{25} +20^\circ$ in EtOH), whereas at 125°/vac. it gives *r*-methylidihydrothebaineisomethine, m.p. 139.5—141.5°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH. (—)-Methylidihydrothebaine-9:10-dihydromethine *Me ether* (*tartrate*, m.p. 106—110°, $[\alpha]_D^{25} +32.3^\circ$ in EtOH; *methiodide*, m.p. 182—183° after softening at about 170°, $[\alpha]_D^{25} +29.1^\circ$ in EtOH) is unchanged by boiling conc. HCl. (X) yields a *methiodide*, m.p. $>230^\circ$, degraded by 40% NaOH to (V) and its (+)-isomeride. When heated at 125° in vac. for 4 days (I) is mainly transformed into the mol. compound, α -methylidihydrothebaine, m.p. 123—124.5°, $[\alpha]_D^{25} +48^\circ$ in EtOH, which could not be hydrogenated. Treatment of its solution in 6N-HCl with NH_4Cl ppts. α -methylidihydrothebaine hydrochloride. Addition of 20% $HClO_4$ to the filtrate from this yields η -methylidihydrothebaine *perchlorate*, $[\alpha]_D^{25} -49^\circ$ in EtOH. The non-cryst. base (XI) is indifferent towards catalytic hydrogenation. δ -Methylidihydrothebaine *perchlorate* $[\alpha]_D^{25} \pm 0^\circ$, gives a base, m.p. 79—83°. Degradation of (XI) is exactly analogous to that of (VII), giving at every step derivatives having the same composition as, but rotatory power opposite to, those of the δ -series with which

compounds having the properties of racemates were formed. η -Methyldihydrothebaineisomethine salicylate, prepared as described for the δ -compound, has m.p. 209—211°, $[\alpha]_D^{25} +14^\circ$ in EtOH; it gives the corresponding $\delta\eta$ -compound, m.p. 190—195° (decomp.), $[\alpha]_D^{25} \pm 0^\circ$ in EtOH. The non-cryst. η -methyldihydrothebaineisomethine is transformed by partly hydrolysed AcCl into hydroxydihydro- η -methyldihydrothebaineisomethine, m.p. 163.5—165.5°, $[\alpha]_D^{25} -23^\circ$ in EtOH (corresponding $\delta\eta$ -compound, m.p. 167—168.5°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH), and 9-dimethylamino-6-methoxy- η -methylthebendiene (XII), m.p. 101—103°, $[\alpha]_D^{25} -34^\circ$ in EtOH ($\delta\eta$ -substance, m.p. 110—112°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH). Boiling 80% NaOH degrades (XII) to (—)-6-methoxy- α -methylthebentriene, m.p. 99—101.5°, $[\alpha]_D^{25} -7.2^\circ$ in EtOH (r-compound, m.p. 91.5—94°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH). (XI) is converted by MeI and 3N-alkali into the Me ether methiodide, degraded by boiling 40% NaOH into (+)-methyldihydrothebaine-methine Me ether methiodide, m.p. 190.5—192°, $[\alpha]_D^{25} -20^\circ$ in EtOH (corresponding r-compound, m.p. 207.5—209.5°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH), and η -methyldihydrothebaineisomethine Me ether methiodide, m.p. 172.5—178°, $[\alpha]_D^{25} +26.4^\circ$ in EtOH. At 155°/vac. for 10 hr. (VII) passes into the bimol. $\delta\omega$ -methyldihydrothebaine (XIII), m.p. 123—124.5°, $[\alpha]_D^{25} -48^\circ$ in EtOH. This is dissolved in 6N-HCl and treated with saturated aq. NH_4Cl , whereby ω -methyldihydrothebaine hydrochloride is pptd. The free base (XIV) has m.p. 86.5—89.5°, $[\alpha]_D^{25} -140^\circ$ in EtOH (perchlorate, $[\alpha]_D^{25} -81^\circ$ in EtOH). Equal wts. of it and the δ -base afford (XIII). Equal wts. of it and (I) afford the racemic $\alpha\omega$ -methyldihydrothebaine, m.p. 179—182°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH. Protracted ebullition of a conc. solution of the perchlorate of (XI) in EtOH leads to the formation of a small proportion of (XIV). ω -Methyldihydrothebaine methiodide is degraded to ω -methyldihydrothebaineisomethine (salicylate, m.p. 161.5—165.5°, $[\alpha]_D^{25} +85^\circ$ in EtOH; $\alpha\omega$ -methyldihydrothebaineisomethine salicylate has m.p. 201—204°, $[\alpha]_D^{25} \pm 0^\circ$ in EtOH). Speculations on the structure of the series are offered. H. W.

Reduction studies in the morphine series.
VII. Thebaine. L. SMALL and G. L. BROWNING, jun. (J. Org. Chem., 1939, 3, 618—637).—Codeine Me ether is converted by NaOEt-EtOH at 100° into thebainone Me enolate (I), m.p. 154—156° after slight softening at 148°, $[\alpha]_D^{25} +9.6^\circ$ in 95% EtOH, which is too readily hydrolysed to permit the isolation of salts. It is converted by warm 3N-HCl into thebainone. Na and boiling EtOH reduce (I) to Δ^8 - α -dihydrothebainone Me enolate (II),

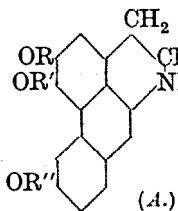


m.p. 164—165.5°, $[\alpha]_D^{25} -115.7^\circ$ in abs. EtOH, transformed into dihydrothebainone by acids; it is also obtained by the catalytic reduction (PtO_2 in abs. EtOH) of (I). isoCodeine Me ether, m.p. 80—82° (salicylate, m.p. 158—159°, $[\alpha]_D^{25} -122.4^\circ$ in H_2O), codeine, isocodeine, and tetrahydrothebaine are recovered nearly quantitatively from the attempted rearrangement with NaOEt and at higher temp. only decomp. products result. Hydrogenation ($\text{Pd}-\text{BaSO}_4$

in 95% EtOH containing NaHCO_3) of thebaine (III) gives dihydrothebainol 6-Me ether, m.p. 140.5—142°, $[\alpha]_D^{25} -23.4^\circ$ in EtOH [fumarate, m.p. 198—201° (decomp.)], $[\alpha]_D^{25} -28.1^\circ$ in H_2O], which does not react with CH_2N_2 but is converted by NPhMe_3OH into a non-cryst. Me ether and (II), which yields a malonate and a fumarate, m.p. 215—217° (decomp.), $[\alpha]_D^{25} -64.4^\circ$ to -39.0° in H_2O , with production of dihydrothebainone fumarate, m.p. $>220^\circ$. (III) is reduced by Na and boiling EtOH to phenolic dihydrothebaine (IV), m.p. 152—154°, $[\alpha]_D^{25} +25.5^\circ$ in EtOH; hydrogenated (PtO_2 in EtOH) to Δ^8 - α -dihydrothebainone Me enolate, m.p. 127—128°, $[\alpha]_D^{25} -8.0^\circ$ in EtOH, readily hydrolysed to dihydrothebainone. (IV) is converted by H_2O saturated with SO_2 at 25° into α -thebainone, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$, m.p. 184—185°, $[\alpha]_D^{25} +158.5^\circ$ in CHCl_3 . An excess of dil. aq. KHSO_4 transforms (IV) at 25° into β -thebainone, $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}\cdot\text{H}_2\text{O}$, m.p. 98—99° after softening at 92°, $[\alpha]_D^{25} +114.9^\circ$ in CHCl_3 [perchlorate (+2 H_2O) (V), m.p. 149—157°, $[\alpha]_D^{25} +67.3^\circ$ in EtOH; hydrobromide, m.p. 168—169° (vac.; decomp.), $[\alpha]_D^{25} +61.1^\circ$ in H_2O ; hydriodide, m.p. 150—155° (vac.; decomp.), $[\alpha]_D^{25} +55.3^\circ$ in H_2O ; picrate, m.p. 172—183° (decomp.), $[\alpha]_D^{25} +43.8^\circ$ in COMe_2 ; non-cryst. oxime and its fumarate, m.p. 220.5° (vac.), $[\alpha]_D^{25} +46.0^\circ$ in H_2O ; non-cryst. semicarbazone and its picrate, m.p. 203—204° (vac.; decomp.)]. Hydrogenation (PtO_2 in EtOH) of (V) and treatment of the product with NH_3 affords β -dihydrothebainone, a non-cryst. liquid, $[\alpha]_D^{25} -48.1^\circ$ in EtOH [hydrochloride, m.p. 245—248° (vac.) after partial melting at 183—190° followed by resolidification, $[\alpha]_D^{25} -34.4^\circ$ in H_2O ; hydrobromide, m.p. 182—185° and, after re-solidification, m.p. 225.5—227.5° (vac.), $[\alpha]_D^{25} -31.5^\circ$ in H_2O ; perchlorate, m.p. 254—255° (vac.), $[\alpha]_D^{25} -32.5^\circ$ in H_2O ; picrate, m.p. 202—215° (vac.; decomp.), $[\alpha]_D^{25} -16.5^\circ$ in COMe_2 ; methiodide, (+2 H_2O) (VI), m.p. 149—154° (vac.); oxime, m.p. 225—226°, $[\alpha]_D^{25} -100.4^\circ$ in EtOH]. Boiling 40% NaOH transforms (VI) into β -dihydrothebainonemethine (VII) [de-N-methyl- β -dihydrothebainone], m.p. 183—184°, $[\alpha]_D^{25} -257.9^\circ$ in EtOH (perchlorate, m.p. 225.5—226° (vac.); picrate, m.p. 164—165° (vac.), $[\alpha]_D^{25} -181.1^\circ$ in COMe_2 ; oxime, m.p. 160—162° (vac.)]. Hydrogenation (PtO_2 in dil. AcOH) of (VII) yields β -dihydrothebainone dihydromethine [dihydrode-N-methyl- β -dihydrothebainone] (VIII), m.p. 177—178° (vac.), $[\alpha]_D^{25} +63.8^\circ$ in CHCl_3 [hydrobromide, m.p. 260—260.5° (vac.), $[\alpha]_D^{25} +24.0^\circ$ in H_2O ; perchlorate, m.p. 232.5—233.5° (vac.), $[\alpha]_D^{25} +23.8^\circ$ in MeOH; picrate, m.p. 203—207° (vac.; decomp.), $[\alpha]_D^{25} +18.2^\circ$ in COMe_2]; its oxime is non-cryst. and does not yield cryst. salts. Successive treatment of (VIII) with MeI in C_6H_6 and boiling 40% NaOH affords β -thebaine, m.p. 189—190°, $[\alpha]_D^{25} +113.6^\circ$ in EtOH (oxime, m.p. 176—177°, $[\alpha]_D^{25} +30.6^\circ$ in EtOH). H. W.

Constitution of tuduranine. K. GOTO and H. SHIRSHIDO (Proc. Imp. Acad. Tokyo, 1939, 15, 8—9; cf. A., 1936, 88; 1937, II, 435).—Tuduranine (I) is 1-3-hydroxy-5:6-dimethoxy-N-noraporphine. Notice is given of the synthesis of the substance A ($\text{R} = \text{R}' = \text{Me}$, $\text{R}' = \text{Et}$), which is shown by the products obtained from it by the Hofmann degradation not to be identical with the Et derivative of natural (I).

The compound **A** ($R = Et$; $R' = R'' = Me$) could be obtained in only very small yield. *r-5:6-Dimethoxy-3-ethoxy-N-ethylnoraporphine ethiodide*, m.p. 186—187°, is converted into *N*-diethyltuduranine *Et* ether ethiodide, new m.p. 194°, and thence into *5:6-dimethoxy-3-ethoxy-8-vinylphenanthrene*, m.p. 108°, identical with the substances derived from the natural alkaloid. H. W.



Delphinine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1939, 127, 361—366).—The seeds of *Delphinium staphisagria*, L., yield to light petroleum delphinine (I), new formula, $C_{33}H_{45}O_9N$, m.p. 198—200°, $[\alpha]_D^{25} +25^\circ$ in abs. EtOH (hydrochloride, m.p. variable, 208—210°). With NaOH-aq. MeOH (I) gives 1 mol. each of BzOH and AcOH, with H_2 -PtO₂ at 3 atm. in EtOH containing a little AcOH gives a *H*₈-derivative, m.p. 192—193° (hydrolysed to hexahydrobenzoic acid instead of BzOH), with KOH at 260° gives NH_2Me , and with $KMnO_4$ -COMe₂ yields the neutral substance, "X 214°" (II) (Keller, A., 1925, i, 831), m.p. 218—220° or 225°. (II) retains the OBz and OAc, but has lost the *N*-Me. An OH is present in (I). R. S. C.

Alkaloids of fumariaceae plants. XVIII. *Fumaria officinalis*, L. R. H. F. MANSKE (Canad. J. Res., 1938, 16, B, 438—444).—The following alkaloids have been isolated: protopine, *dl*-tetrahydrocoptisine, cryptocavine, aurotensine, and possibly sinactine, m.p. 177°, $[\alpha]_D^{23} -78.9^\circ$ in $CHCl_3$. Two new alkaloids have also been obtained: $C_{21}H_{23}O_5N$, m.p. 177°, non-phenolic, containing 2 OMe, and $C_{26}H_{19}O_6N$, m.p. 256°, phenolic and probably a phthalide isoquinoline alkaloid. A neutral substance, $C_{11}H_{10}O_3$, m.p. 152°, has been isolated. The significance of alkaloid structure in an evolutionary series of plants is discussed. F. R. S.

Lobinaline, an alkaloid from *Lobelia cardinalis*, L. R. H. F. MANSKE (Canad. J. Res., 1938, 16, B, 445—448).—Only one alkaloid, lobinaline, $C_{25}H_{38}ON_2$, m.p. 94—95°, $[\alpha]_D^{24} +22.3^\circ$ in $CHCl_3$ [monohydrochloride (+1.5H₂O), m.p. 220°], has been isolated. Oxidation with $KMnO_4$ yields BzOH in amount insufficient for the presence of two monosubstituted C_6H_5 nuclei. F. R. S.

Calycanthine. III. Degradation experiments. L. MARION and R. H. F. MANSKE (Canad. J. Res., 1938, 16, B, 432—437).—Dehydrogenation of calycanthine (I) by either Se or Zn gives a base, $C_{16}H_{10}N_2$ (?), m.p. 307°, and 4-carbolone; this supports the structure for (I) previously suggested (A., 1931, 855). Reduction (P-HI) of (I) affords quinoline and oxidation $[Hg(OAc)_2]$ results in the formation of a base with loss of 2 H. $o-C_6H_4(CO)_2O$ and (I) yield 12:13-benzcanthin-11-one (?), m.p. 227°, also obtained from tryptamine and $o-C_6H_4(CO)_2O$. Tryptamine and $(CH_2CO)_2O$ give 3:4:5:6:12:13-hexahydro-3-hydroxycanthin-11-one (?), m.p. 172°. The phenyl-carbamyl derivative of (I) has m.p. 252°. Methylation of (I) with MeI gives products containing 1, 2, and 3 O,

which are not homogeneous; the N is eliminated as NH_2Me . F. R. S.

Alkaloids of *Salsola richteri*. IV. Salsolidine. N. PROSKURNINA and A. OREKHOV (Bull. Soc. chim., 1939, [v], 6, 144—146; cf. A., 1937, II, 265, 394; 1938, II, 117).—*d*- and *l*-Salsolidine each exist in two forms, m.p. 47—48° and 71—73°, produced respectively by distilling in vac. and by crystallising from H_2O ; they give the same salts and have the same $[\alpha]$. The free racemic base is said to absorb CO_2 far more rapidly than the active isomerides, and the base, m.p. 117—119°, previously reported was the carbonate. A. Li.

Behaviour of alkaloids to filtered ultra-violet light.—See A., 1939, I, 178.

Arsenic derivatives of phenylmethylcarbinol. C. K. BANKS and C. S. HAMILTON (J. Amer. Chem. Soc., 1939, 61, 357—360).—3:4:1- $NO_2 \cdot C_6H_3(OH) \cdot COMe$ (modified prep.) and Raney Ni- H_2 give 3-amino-4-hydroxyacetophenone, m.p. 98° [hydrochloride, m.p. >250° (decomp.)], which yields (Bart) 4-hydroxy-3-arsinoacetophenone, m.p. 225°, and thence (SO₂) 2-hydroxy-5-acetylphenylarsenious oxide, m.p. 104°, and 2:2'-dihydroxy-5:5'-diacetylarsenobenzene, m.p. 193—198° (decomp.), but attempts to reduce the CO to CH-OH lead to removal of AsO_3H_2 . 3-Amino-4-methoxyacetophenone, m.p. 85° [hydrochloride, m.p. 170° (decomp.)], similarly prepared, gives similarly 4-methoxy-3-arsinoacetophenone (I), m.p. 212°, 2-methoxy-5-acetylphenylarsenious oxide, m.p. 294° (decomp.), and 2:2'-dimethoxy-5:5'-diacetylarsenobenzene, m.p. 168° (decomp.). H_2 -Raney Ni reduces (I) in aq. NaOH at 80°/2.67 atm. to *Na H* 5-methoxy-2- α -hydroxyethylphenylarsinate (II), m.p. >300° (decomp.); decomp. of (II) by acid leads to loss of H_2O and formation of a polymeride, m.p. 295—320°, of 4-aminostyrene-3-arsinic acid, but Ac_2O yields α -4-methoxy-3-arsinophenylethyl acetate, m.p. ~320° (decomp.), and reduction affords 2:2'-dimethoxy-5:5'-di-(α -hydroxyethyl)arsenobenzene, m.p. 245—250° (decomp.) [diacetate, m.p. 268° (decomp.)]. The oxime, m.p. 200°, of (I) with H_2 -Raney Ni in *N*-NaOH at 80°/3 atm. gives much (I) and a polymeride, m.p. >300°, of 2:2'-dimethoxy-5:5'-divinylarsenobenzene with small amounts of α -4-methoxyphenylethylamine-3-arsinic acid, m.p. 248° (decomp.) (Ac derivative, m.p. >300°), di- [Ac derivative, m.p. 278° (decomp.)] and tri- α -4-methoxy-3-arsinophenylethylamine, m.p. 205°. 2:2'-Dimethoxy-5:5'-di-(α -oximinoethyl)arsenobenzene sublimes at 135°. R. S. C.

Arsenicals derived from *m*-aminophenol. A. E. BEGUIN and C. S. HAMILTON (J. Amer. Chem. Soc., 1939, 61, 355—357).—4:2:1- $CO_2Et \cdot NH \cdot C_6H_3(OH) \cdot AsO_3H_2$ with PCl_3 in Et_2O , followed by H_2O , gives 4-carbethoxyamino-2-hydroxyphenylarsenious oxide, m.p. 159° (*Na* salt), which with $(CH_2)_2O$ and KOH in EtOH gives β -3-carbethoxyamino-6-arsinophenoxyethyl alcohol (I), m.p. 233°, reduced to 4:4'-di(carbethoxyamino)-2:2'-di-(β -hydroxyethoxy)arsenobenzene, m.p. 222°. 4:2:1- $NH_2 \cdot C_6H_3(OH) \cdot AsO_3H_2$ with Ac_2O -AcOH gives 4-acetamido-2-hydroxyphenylarsinic acid, decomp. 266°, and with $ClCO_2Pr^a$ and 2*N*-NaOH gives 4-carbo-

n-propoxyamino-2-hydroxyphenylarsinic acid, decomp. 220°, and thence the derived arsenious oxide, m.p. 198°. 4-Carbobenzylxyamino-2-hydroxyphenylarsinic acid (II), decomp. 223°, is similarly prepared and yields the derived arsenious oxide, m.p. 217°, β -3-carbobenzylxyamino-, m.p. 235°, and thence (0.5N-NaOH) β -3-amino-6-arsinophenoxyethyl alcohol, m.p. 164°. With propylene oxide and KOH-EtOH (II) gives β -3-carbobenzylxyamino-, m.p. 176°, and thence β -3-amino-6-arsinophenoxyisopropyl alcohol, softens at 159°, which with ClCO_2Et gives β -3-carbethoxyamino-6-arsinophenoxyisopropyl alcohol (III), m.p. 185°. $m\text{-NO}_2\text{-C}_6\text{H}_4\text{[CH}_2\text{]}_2\text{OH}$ and Raney Ni- H_2 at 2.67 atm. yield β -*m*-aminophenoxyethyl alcohol, an oil (N-Ac, m.p. 106°, and N- CO_2Et -derivative, m.p. 56°), also obtained from (I) by Raney Ni- H_2 in COMe_2 at 2.67 atm. β -*m*-Carbethoxyaminophenoxyisopropyl alcohol, b.p. 225°/11 mm., is similarly prepared from the NO_2 -compound or (III). R. S. C.

Relation between the constitution of 4-*p*-arsinoanilinonaphtha-1 : 2-quinone-8-sulphonic acid (2654N) and its therapeutic action. E. A. H. FRIEDHEIM (Arch. Sci. phys. nat., 1938, [v], 20, Suppl., 73—78).—The trypanocidal action of 2654N depends on its 1 : 2-quinone structure. Thus, the leuco-derivative is slightly more toxic, but about as trypanocidal; the 2-Bz and 2- CO_2Et -derivatives (which are 1 : 4-quinone-imines) are slightly more toxic and considerably less trypanocidal; the dibenzoate of the leuco-derivative is not trypanocidal, being excreted unchanged, but the $(\text{CO}_2\text{Et})_2$ -derivative has some effect, being partly hydrolysed in the body; the azine [obtained by condensation with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$] and the sulpho- and arsino-azines (obtained by condensing with *o*-phenylenediamine-3-sulphonic and -3-arsinic acid, respectively) are not trypanocidal, but are very toxic, particularly the first-named (max. dose tolerated = 0.1 g. per kg.). The isomeric red 1 : 4-quinone (2-*p*-arsinoanilinonaphtha-1 : 4-quinone-8-sulphonic acid, obtained from arsanilic acid and naphtha-1 : 2-quinone-4 : 8-disulphonic acid in HCl, from naphtha-1 : 4-quinone-8-sulphonic acid, or from 2654N by dil. HCl) has no trypanocidal action and is very toxic (max. dose tolerated = 0.05 g. per kg.). 4-2'-Hydroxy-5'-arsinoanilinonaphtha-1 : 2-quinone-8-sulphonic acid (obtained from naphtha-1 : 2-quinone-4 : 8-disulphonic acid and 3-amino-4-hydroxyphenylarsinic acid) has low toxicity (max. dose tolerated = 3 g. per kg.), but only slight trypanocidal action (min. curative dose = 0.7 g. per kg.); it is excreted in the bile, whereas 2654N is eliminated by the kidneys. 2654N is partly reduced to the leuco-derivative before excretion, but the latter, when administered, is partly oxidised before excretion. R. S. C.

Decomposition of unsymmetrical organomercuric compounds. Method of establishing the relative electronegativities of organic radicals. M. S. KHARASCH, R. R. LEGAULT, and W. R. SPROWLS (J. Org. Chem., 1938, 3, 409—413).—Cleavage experiments with HCl and Hg compounds show that the 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2$ radical is less electronegative than $m\text{-C}_6\text{H}_4\text{Cl}$ and more electronegative than CH_2Ph .

2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2$ is less electronegative than $m\text{-C}_6\text{H}_4\text{Cl}$ and more so than Me. Direct substitution decreases the electronegativity of Ph. Introduction of a second Cl in the aromatic nucleus decreases still more the electronegativity of the $\text{C}_6\text{H}_4\text{Cl}$ radicals. All substituted aromatic radicals thus far observed are more electronegative than any of the aliphatic radicals. Compounds, HgRCl , are described in which $\text{R} = 2 : 4\text{-C}_6\text{H}_3\text{Cl}_2$, m.p. 196°, 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 205°, 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Cl}_3$, m.p. 184°, CH_2Ph , m.p. 104°, Ph, m.p. 250—251°, $o\text{-C}_6\text{H}_4\text{Cl}$, m.p. 147°, $m\text{-C}_6\text{H}_4\text{Cl}$, m.p. 208°, and Me, m.p. 170°. Also substances HgRR' , in which the pairs of radicals are: Ph, 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2$; $o\text{-C}_6\text{H}_4\text{Cl}$, 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 152—162°; $m\text{-C}_6\text{H}_4\text{Cl}$, 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 136—142°; CH_2Ph , 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 100—147°; Ph, 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 120° after softening at 95°; $m\text{-C}_6\text{H}_4\text{Cl}$, 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2$, m.p. 134—138°; 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2$, Me, m.p. 75—80°; CH_2Ph , $m\text{-C}_6\text{H}_4\text{Cl}$, an oil. H. W.

Reactivity of organo-lithium compounds. E. MÜLLER and T. TÖPEL (Ber., 1939, 72, [B], 273—290).—LiBu and O_2 give Bu°OH in 75% yield. An intermediate peroxide is probably formed since the Li salt of 1 : 2 : 3 : 4-tetrahydronaphthalene peroxide and LiPh give LiOPh and Li 1 : 2 : 3 : 4-tetrahydronaphth-1-oxide. LiPh and O_2 give about 65% of Ph_2 , 18% of PhOH, and 6% of $\text{CHPhMe}\cdot\text{OH}$ formed by intervention of the solid. Only 4% of Ph_2 is formed during the prep. of the reagent. Analogously $p\text{-LiC}_6\text{H}_4\text{Ph}$, readily obtained from $p\text{-C}_6\text{H}_4\text{PhCl}$, gives >85% of quaterphenyl, about 3% of $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$, and about 7% of Ph_2 . $p\text{-LiC}_6\text{H}_4\text{Me}$ and O_2 afford $p\text{-cresol}$ (37%), pp' -ditolyl (35%), PhMe (8%), and $p\text{-tolylmethylcarbinol}$ (corresponding phenylurethane, m.p. 92°) (yield 11%). From $m\text{-LiC}_6\text{H}_4\text{Me}$ the yields of mm' -ditolyl, b.p. 280—284°, $m\text{-cresol}$, $m\text{-tolylmethylcarbinol}$ (phenylurethane), and PhMe are respectively 17%, 31%, 22%, and 12% whilst from $o\text{-LiC}_6\text{H}_4\text{Me}$ the yields of oo' -ditolyl, $o\text{-cresol}$, $o\text{-tolylmethylcarbinol}$ (phenylurethane, m.p. 79—80°), and PhMe are 5%, 54%, 28%, and 60% respectively. $p\text{-LiC}_6\text{H}_4\cdot\text{OMe}$ and O_2 give about 26% of pp' -dianisyl, about 35% of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, and about 36% of PhOMe. Under mild conditions the formation of $p\text{-LiC}_6\text{H}_4\cdot\text{OMe}$ proceeds normally since the product is transformed by COPh_2 into diphenylanisylcarbinol, whence diphenylanisylcarbinyl chloride, m.p. 122°. Under more drastic conditions reaction occurs between $p\text{-LiC}_6\text{H}_4\cdot\text{OMe}$ and unchanged $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ with formation of 2 : 4 : 1- $\text{LiC}_6\text{H}_3\text{Br}\cdot\text{OMe}$. 2 : 1 : 4- $\text{LiC}_6\text{H}_3(\text{OMe})_2$ and O_2 give 60% of the initial material and 40% of 2 : 1 : 4- $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$; the formation of a dimeric compound could not be detected. $\text{LiC}_{10}\text{H}_7\cdot 1$ and O_2 yield exclusively $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, the small amount of $(\text{C}_{10}\text{H}_7)_2$ found being formed during the prep. of the reagent. Similarly Li *ar*- α -bromo-tetrahydronaphthalene gives solely *ar*- α -tetrahydronaphthol. Li styryl affords a polymeric compound containing O which has not been identified but no diphenylbutadiene. LiCH_2Ph gives mainly $\text{CH}_2\text{Ph}\cdot\text{OH}$. An explanation of the unique behaviour of LiPh and $p\text{-LiC}_6\text{H}_4\text{Ph}$ is advanced. NaPh could not be caused to react with O_2 in Et_2O . 9-Bromoanthracene and Li rapidly give Li_2 9 : 10-dihydro-

anthracene (the isolation of the intermediate Li 9-anthryl appearing impossible). With NHPhEt it yields 9:10-dihydroanthracene and with CO_2 9:10-dihydroanthracenedicarboxylic acid. An additive compound is also formed from Li and 9:10-dibromoanthracene.

9-Bromo-1—8-octahydroanthracene and Li rapidly give 1—8-octahydroanthracene but the reaction cannot be stopped at the intermediate stage. 9-Bromophenanthrene reacts very slowly with Li; the Li compound immediately decomposes the Et_2O and the phenanthrene so formed adds to metal atoms at $\text{C}_{(9)}$ and $\text{C}_{(10)}$. During the prep. of $\text{LiC}_{10}\text{H}_7$ -1 and $p\text{-LiC}_6\text{H}_4\text{Ph}$ considerable amounts of hydrocarbon are formed by intervention of Et_2O ; these add metallic Li with production of H_2 -compounds. The incidence of the change is indicated by a change in colour and the action must be immediately interrupted at this stage if good yields of organo-Li compounds are to be obtained. Determination of yield by titration with acid is untrustworthy and should be replaced by reaction with ketones or BuBr. The applicability of Li compounds is restricted by their great activity towards Et_2O and $(\text{CH}_3\text{O})_2$. *cycloHexane*-1:4-dione and $p\text{-LiC}_6\text{H}_4\text{Ph}$ give the corresponding carbinol, which loses 2 H_2O during the reaction, yielding dihydroquinquephenyl; this becomes partly oxidised during manipulation so that ultimately the *quinhydrone*, m.p. 362—363°, from quinquephenyldihydroquinquephenyl results, and is dehydrogenated (Se) to quinquephenyl, m.p. 388—389°. Bis- β -dimethylbutadienebenzoquinone and LiPh afford bis-(2:3-dimethylbutadiene)benzo-9:10-diphenylquinol, m.p. 223—224°, dehydrogenated by Se at 270° to 9:10-diphenyl-2:3:6:7-tetramethylantracene, m.p. 284—285°.

H. W.

Arylated chlorostibiates and chlorostibanates. P. PFEIFFER and P. SCHMIDT (J. pr. Chem., 1939, [ii], 152, 27—44).—*m*-Chlorophenylstibinic acid (prep. from $m\text{-C}_6\text{H}_4\text{ClNH}_2$ described) is dissolved in conc. HCl - MeOH - H_2O containing a trace of KI and reduced by SO_2 to *Sb m-chlorophenyl oxide*, which with $\text{C}_5\text{H}_5\text{N}$ in AcOH -conc. HCl gives *pyridinium m-chlorophenylotrichlorostibiate*, m.p. 117—118°, and with quinoline yields the corresponding *quinolinium* compound, m.p. 118—119° (slight decomp.). α -Naphthylidiazonium tetrachlorostibiate is converted by 10% NaOH at room temp. into α -naphthylstibinic acid, whence *Sb α -naphthyl chloride*, m.p. 105°, and *pyridinium α -naphthylotrichlorostibiate*, m.p. (indef.) 90°. Analogously, $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ affords successively β -naphthylidiazonium tetrachlorostibiate, decomp. 100—120°, β -naphthylstibinic acid, *Sb β -naphthyl oxide*, m.p. (indef.) 135—140°, and *pyridinium β -naphthylotrichlorostibiate*. The following *pentachlorostibanates* are obtained by treating a solution of the requisite stibinic acid with the requisite base dissolved in conc. HCl : *pyridinium phenyl-*, m.p. 105° (decomp.); NH_4 *m-chlorophenyl-*, m.p. >240°; *pyridinium m-chlorophenyl-*; *quinolinium m-chlorophenyl-*; NH_4 α -naphthyl-, m.p. >240°, sublimes at 200°; *pyridinium α -naphthyl-*, m.p. 187—189°; *pyridinium β -naphthyl-*, m.p. 200—202° (decomp.); *quinolinium β -naphthyl-*, m.p. 174—176° (decomp.), after softening at 110° and darkening at ~140°. *Pyridinium β -naphthylpentabromostiban-*

ate, m.p. 193—195°, and *pyridinium diphenylotetrachlorostibanate*, decomp. ~265°, are described.

H. W.

Organo-silicon synthesis. II. Reactions of aryl Grignard reagents with silicon halides. W. C. SCHUMB and C. M. SAFFER, jun. (J. Amer. Chem. Soc., 1939, 61, 363—366; cf. A., 1938, II, 476).—The reactions with SiCl_4 , Si_2Cl_6 , Si_3Cl_8 , Si_4OCl_6 , SiBr_4 , Si_2Br_6 , Si_2OBr_4 , and $\text{Si}_3\text{O}_2\text{Br}_8$ in the conventional way yield only partly substituted silanes, but by the high-temp. modification of the Grignard reaction hexa-aryl-disilanes and -disiloxanes may be prepared in fairly good yields. The reaction cannot be extended to the prep. of compounds containing the Si-Si-Si or Si-O-Si-O structures, or of tetra-*o*-substituted phenylsilanes. The prep. of *hexa-p-tolyldisilane*, m.p. 345°, and *hexa-n-propyldisilane*, b.p. 114°/3 mm., is described.

E. S. H.

Formation of organo-metalloidal and similar compounds by micro-organisms. VII. Dimethyl telluride. M. L. BIRD and F. CHALLENGER (J.C.S., 1939, 163—168; cf. A., 1939, II, 12).—Air aspirated through cultures of *Scopulariopsis brevicaulis*, Saccardo (strain Washington 2), on bread or a 2% glucose Czapek-Dox solution containing K_2TeO_3 and passed through aq. HgCl_2 - HCl gives Me_2Te , HgCl_2 . Similarly, TeMe_2 is obtained with other strains of *S. brevicaulis* and with *Penicillium notatum*, Westling, and identified by absorption in $\text{EtOH-CH}_2\text{PhCl}$ followed by treatment with Na picrate, when *benzyl-dimethyltelluronium picrate*, m.p. 121°, is obtained. Similarly, *P. notatum* and *P. chrysogenum* with Na_2SeO_3 or Na_2SeO_4 on aq. bread culture yield Me_2Se . Interaction of Me_2Te with $\text{CH}_3\text{Br-CO}_2\text{Et}$ and with CH_3BzBr in Et_2O or EtOH yields respectively *dimethylcarbethoxymethyl-*, m.p. 137.5, and *phenacyldimethyl-telluronium bromide*, m.p. 90—91°. J. D. R.

Elastoidin. R. ENGELAND and A. BASTIAN (Compt. rend., 1938, 207, 945—947).—Elastoidin (from *Carcharias glaucus*) with boiling 25% H_2SO_4 affords a hydrolysate from which the Cu salts of NH_2 -acids are isolated by Brazier's method. Extraction of these salts with MeOH , followed by treatment with H_2S , gives glycine, alanine, serine, hydroxyproline, a compound, $\text{C}_7\text{H}_{15}\text{O}_5\text{N}$, and a diaminodihydroxyvaleric acid (?). From the phosphotungstic acid ppt. of the hydrolysate, the betaine of dihydroxyornithine is isolated.

J. L. D.

Nature of the cyclol bond. I. LANGMUIR and D. WRINCH (Nature, 1939, 143, 49—52).—The nature of the cyclol bond, the making and breaking of which is a prototropic tautomerism, is discussed in relation to the properties of globular proteins and to the cyclol theory.

L. S. T.

Organic chemistry of proteins. J. OVERHOFF (Chem. Weekblad, 1939, 36, 115—122).—A review.

S. C.

Use of semi-micro-technique in organic chemistry. N. D. CHERONIS (J. Chem. Educ., 1939, 16, 28—34).—A simple micro-condenser, distillation tubes, simple arrangements for fractionating, refluxing, distilling, extraction, separation, filtration, and

measuring are described, and their use is illustrated by the prep. of PhNO_2 , PhEt , *cyclohexene*, BzOH , etc.

L. S. T.

Determination of carbon in organic compounds. A. K. PARPART and A. J. DZEMIAN (*Ind. Eng. Chem. [Anal.]*, 1939, 11, 107).—The combustion vessel employed in the method of Van Slyke *et al.* (A., 1933, 1314) is modified to obviate the possibility of leaks.

F. N. W.

Micro-titrimetric dry combustion method for carbon. II. Modified titration vessel. R. H. NAGEL (*Mikrochem.*, 1939, 26, 22–24).—A modified absorption and titration vessel is described suitable for use with the micro-method described by Schmitt and Niederl (A., 1938, II, 209). Provision is made for alternate washing of the cell after use with H_2O and EtOH , thereby eliminating the necessity of steaming out after each usage. Attempts to develop a semi-micro-method on the same principles were unsuccessful.

J. W. S.

Simplified combustion tube filling for micro-determinations of carbon and hydrogen. J. B. NIEDERL and V. NIEDERL (*Mikrochem.*, 1939, 26, 28).—It is not necessary to use PbCrO_4 in micro-combustions when metallic Ag is present, as the latter absorbs the oxides of S quantitatively.

J. W. S.

Modifications of Pregl's method for the micro-analytical determinations of carbon and hydrogen in the humid summer atmosphere of a tropical country. M. C. NATH (*Mikrochem.*, 1939, 26, 165–169).—Pregl's method yields low vals. for C in the hot humid atm. of India. Under such conditions it has been found necessary to extend the period of combustion from 10 to 15 min., and to increase the O_2 current to 4–5 c.c. per min. Escape of gas through rubber connexions is minimised by cleaning these with glycerol on a glass rod, the glycerol being removed again with a dry rod. No cotton is used inside the tubes. Connexions between the combustion and CaCl_2 tubes are renewed after each combustion, and other rubber parts after three combustions. Before weighing, the capped absorption tubes are allowed to come into equilibrium with the atm. in a balance room, the moisture content of which is kept const. Blank tests are run before and after each combustion.

J. W. S.

Micro-combustion analysis of very volatile liquids. E. EIGENBERGER (*Mikrochem.*, 1939, 26, 273–276).—In the method recommended the liquid is contained in a small capillary tube itself inserted into a projection in the combustion tube which can be cooled. The tip of the capillary tube is blown out by heating with an electrically-heated wire. The arrangement is equally suitable for determination of C, H, and N.

J. W. S.

Use of lead peroxide in micro-elementary analysis. J. LINDNER (*Mikrochem.*, 1938, 25, 197–207; cf. A., 1933, 80).—Data showing that different preps. of PbO_2 possess different absorptive powers for NO_2 , that this absorption increases with a decrease in particle size, and that the hygroscopic effect increases to an even greater extent are discussed. Previous conclusions concerning the efficacy of

PbO_2 and the difficulty of ascertaining the correct amount of the prep. to be used are supported. More active PbO_2 preps. make it possible to effect a satisfactory removal of NO_2 , but a smaller interference in the H_2O determination does not necessarily follow. The use of a smaller amount of PbO_2 , frequently renewed, instead of the universal filling leads to an improvement in the H_2 determination, but one of the advantages of using PbO_2 is thereby lost. Metallic Cu is preferable to PbO_2 since it decomposes the NO_2 completely, and produces no interference in the H_2 determination.

L. S. T.

Discussion of important and difficultly-accessible microchemical literature. F. CANAL (*Mikrochem.*, 1938, 25, 182–183).—The catalytic method of Contardi and Ferri (A., 1934, 1375) for the determination of C and H, and the electrical method of Contardi and Erighian (A., 1937, I, 152) for the semi-micro-determination of N are described.

L. S. T.

Semi-micro-method for determining carbon and hydrogen in organic compounds. G. INGRAM (*J.S.C.I.*, 1939, 58, 34–37).—The micro-method of Friedrich (cf. A., 1932, 71, 921) is adapted for use as a semi-micro-method (10–21 mg. of substance), involving a modified tube filling on which all types of substances can be analysed. The PbO_2 is contained in a porcelain boat, the oxidation filling being in a CuO tube, which allows the PbO_2 to be changed when used up. The complete analysis, which takes <1 hr., is carried out in a stream of O_2 , Pregl's absorption tubes being used. The method is simple and quick, taking <1 hr. for each analysis.

Standard solutions in quantitative organic micro-analysis. J. B. NIEDERL, V. NIEDERL, and M. EITINGON (*Mikrochem.*, 1938, 25, 143–150).—0.01N- $\text{KH}(\text{IO}_3)_2$ can, with advantage, be substituted for 0.01N- HCl in all the acidimetric and alkalimetric titrations used in org. micro-analysis. It also serves as a standard for the iodometric titrations. No change in titre could be detected after storage for 6 months. For the precision required in org. analysis (5 in 1000), 0.01N- NaOH requires re-standardisation monthly and 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$ weekly. Details of the prep. of the $\text{KH}(\text{IO}_3)_2$, the standard solutions of $\text{KH}(\text{IO}_3)_2$, NaOH , and $\text{Na}_2\text{S}_2\text{O}_3$, and the indicator solutions of phenolphthalein, Me-red, and starch are given. The high mol. wt. of the iodate renders the use of a micro-balance unnecessary. Test data for the determination of the equiv. of 3 org. acids, and the determination of NH_3 , S, I, Cl, and Br are recorded. A device for steaming-out conical flasks is illustrated.

L. S. T.

Ultra-micro-Kjeldahl technique.—See A., 1939, I, 214.

Determination of halogens in organic compounds. H. B. FELDMAN and L. POWELL (*Ind. Eng. Chem. [Anal.]*, 1939, 11, 89–90).—Reduction by Cook and Cook's modification (A., 1933, 731) of the Stepanow technique followed by titration with 0.1N- AgNO_3 using dichlorofluorescein for Cl and eosin for Br and I as absorption indicators affords accurate results for a variety of org. halides.

F. N. W.

Determination of chlorine in organic compounds. V. DOSTÁL (Chem. Listy, 1939, 33, 78—79).—The material is heated with KOH-KNO₃ mixture in a hard glass tube, and Cl' is determined in the melt by the Volhard method. R. T.

Hygroscopic substances in micro-analysis.—See A., 1939, I, 223.

Determination of water in organic liquid mixtures. R. A. DAY, jun., and R. N. PEASE (J. Amer. Chem. Soc., 1939, 61, 524—525).—H₂O in org. liquids is determined by adding powdered, anhyd. CuSO₄, filtering, washing with liquid C₄H₁₀, and determining the gain in wt. of the CuSO₄. R. S. C.

Micro-technique of organic qualitative analysis. F. SCHNEIDER and D. G. FOULKE (Ind. Eng. Chem. [Anal.], 1939, 11, 111—113; cf. A., 1938, II, 423).—Reactions capable of classifying compounds containing C, H, and O, as aldehyde, carbohydrate, phenol, anhydride and lactone, ketone, and alcohol are recorded together with micro-methods for the titration of acids and hydrolysis of esters. F. N. W.

Pyridine-acetic anhydride method for determining hydroxyl: preparation of pyridine of suitable quality. H. N. WILSON and W. C. HUGHES (J.S.C.I., 1939, 58, 74—77).—The method of determining OH by boiling with excess of Ac₂O in C₅H₅N, to acetylate the OH, the excess of AcOH being subsequently determined, will give accurate results only if the C₅H₅N is freed from certain impurities and contains 0.3—0.5% of H₂O, to prevent reaction between the C₅H₅N and Ac₂O. Methods of purifying "technical pure" C₅H₅N were evolved, and a specification for suitable C₅H₅N is appended.

Nitroprusside test for ·SH and ·S·S·.—See A., 1939, III, 344.

Determination of ethylene. B. E. CHRISTENSEN, E. HANSEN, and V. H. CHELDELIN (Ind. Eng. Chem. [Anal.], 1939, 11, 114—116).—A micro-method (for which an extractor, purification train, and reaction flask are described) based on the bromination method of Davis *et al.* (B., 1931, 324), capable of determining 0.001—0.06 c.c. of C₂H₄ in a total vol. of 35—40 c.c., is described. The C₂H₄ contents of a no. of fruit and vegetable tissues are recorded. F. N. W.

[Azides. X.] **p-Bromobenzazide** as a reagent for the identification of alcohols. P. P. T. SAH and K. Y. TAO (Rec. trav. chim., 1939, 58, 12—16).—p-Bromobenzazide (A., 1936, 1006) with the following alcohols in boiling petroleum at 80—120° gives p-bromophenylurethanes (m.p. in parentheses): MeOH (125°; cf. lit.); EtOH (84°; cf. lit.); PrⁿOH (77—78°); PrⁱOH (102—104°); BuⁿOH (64—65°); BuⁱOH (96—98°); n-C₅H₁₁OH (76—77°); CH₃CH₂OH (54—55°); n-C₆H₁₃OH (75°); n-C₇H₁₅OH (83—84°); iso-C₇H₁₅OH (65—66°); n-C₈H₁₇OH (78—79°); n-C₉H₁₉OH (73—74°); n-C₁₀H₂₁OH (79°); CH₃CH₂CH₂OH (65°); CH₃PhOH (123—124°); furfuryl alcohol (105—106°); cyclohexanol (113—114°); 4-methylcyclohexanol (160—161°); benzoin (122°); menthol (114°); cholesterol (175—176°); borneol (116—

117°); (CH₂OH)₂ (194°); glycerol [229° (decomp.)]; CH₂Cl·CH₂·OH (88—89°); and CH₂Br·CHBr·CH₂·OH (93—94°). E. W. W.

Determination of linalool, cineole, and terpineol. T. IKEDA and S. TAKEDA (J. Chem. Soc. Japan, 1936, 57, 442—448).—40 g. of the material are heated with 1 g. of ZnCl₂ which has been dried for 1 hr. at 156° and 50 c.c. of xylene at 195—200° for 2 hr., and the H₂O liberated by the dehydration of the linalool, cineole (I), or terpineol is collected and measured. For (I) 3 hr. heating is necessary. A blank must be run to determine the H₂O retained by the ZnCl₂, and a correction applied. CH. ABS. (e)

Application of drop analysis to the investigation of medicinal materials. VII. Detection of polyhydroxy-compounds. O. FREHDEN and K. FÜRST. VIII. Detection of aldehydes with stable reagent paper. O. FREHDEN and C. H. HUANG (Mikrochem., 1939, 26, 36—38, 39—40).—VII. The test for HCO₂H (following abstract) can be applied to detection of polyhydric alcohols, which are first oxidised to HCO₂H by NaIO₄ and H₂SO₄. The HCO₂H is oxidised to CO₂ by Br-H₂O and detected by the turbidity produced by the gas in aq. Ba(OH)₂. The reaction permits detection of 3—5 µg. of polyhydroxy-compounds. Aldehydes other than CH₂O do not interfere with the test.

VIII. Malachite-green (0.8 g.) is dissolved as the leuco-base by addition of Na₂SO₃ (3 g.) and after addition of further Na₂SO₃ (2 g.) the solution is filtered and imbibed on thin test paper, which is allowed to dry in the cold. A drop of test solution placed on the colourless dry test paper produces a green spot if an aldehyde is present. The reaction is favoured by the fine state of distribution of the leuco-base on the paper. The solutions must be neutral, as both acid and alkali cause colour changes. The method is capable of detecting 20—300 µg. of aldehyde. J. W. S.

Application of drop analysis to the investigation of medicinal materials. Selective test for formic acid. O. FREHDEN and K. FÜRST (Mikrochem., 1938, 25, 256—257).—The test, based on the reaction HCO₂H + Br₂ = 2HBr + CO₂, permits the detection of 2.5 µg. of HCO₂H. A few drops of solution are treated with aq. Br until yellow in colour, and the solution is heated to boiling. The evolved gases are passed into saturated aq. Ba(OH)₂ protected from atm. CO₂ by a layer of paraffin. The small amounts of HBr and Br which also distil do not interfere with the test. L. S. T.

Determination of fumaric and maleic acids. S. C. GANGULY (J. Indian Chem. Soc., 1938, 15, 611—614).—The KBr-KBrO₃-HgSO₄ method (A., 1937, I, 314; 1938, II, 210) may be used successfully to determine maleic or fumaric acid, in presence of (CH₂·CO₂H)₂ and Na₂HPO₄. E. W. W.

Iodometric determination of acetone by a turbidimetric method. E. K. NIKITIN and M. E. EGOROVA (Zavod. Lab., 1938, 7, 1363—1367).—1 ml. of 15% I in KI and 1 ml. of 10% KOH are added to 1 ml. of 5% aq. COMe₂, and the time *t*₁ elapsing before appearance of turbidity is noted. An equal vol. of

H₂O is added to the aq. COMe₂, and the experiment is repeated (time = t_2). Finally, the time t required for development of turbidity in the unknown solution is determined. The [COMe₂] is then given by $(x + c)/2$, where $x = c\{1 + (t - t_1)/(t_2 - t_1)\}$, and c is the [COMe₂] of the standard solution. A second, more dil. standard COMe₂ solution (0.01%) is used, with 0.2% instead of 10% KOH, for comparison with very dil. COMe₂ solutions. R. T.

Determination of water in acetone. R. GASPART and L. GILLO (Bull. Soc. chim. Belg., 1938, 47, 933–939).—The presence of an absorption band at 3500 cm.⁻¹, traced to the H₂O-COME₂ complex, permits the spectroscopic determination of 1 part of H₂O in 100,000 parts of COMe₂ with a precision of 0.5%. E. S. H.

Use of periodate in the volumetric determination of polyhydric alcohols and reducing aldoses (monosaccharides), and the determination of periodate and iodate in presence of each other. **Use of periodate in the volumetric determination of ketoses (monosaccharides).** (A) P. FLEURY. (B) F. RAFFAPORT (Mikrochem., 1938, 25, 263–265, 265–266; cf. A., 1937, II, 530; 1938, II, 219).—(A) Attention is directed to the author's previous work on this subject.

(B) The method of Fleury differs in principle and in execution. L. S. T.

Micro-method for the determination of the isopropylidene group in sugar derivatives. D. J. BELL and K. HARRISON (J.C.S., 1939, 350).—The COMe₂ derivative is steam-distilled in N-H₂SO₄, and the COMe₂ is determined. An apparatus is described by which 1 mg. of COMe₂ may be determined with an accuracy of $\pm 1\%$. J. D. R.

Determination of pentose especially in adenylic acid derivatives. W. MEJBAUM (Z. physiol. Chem., 1939, 258, 117–120).—Free and/or combined pentose (1–20 μ g.) is determined by adding to 0.5 c.c. of the solution 0.5 c.c. of fresh Bial's reagent (5 mg. of orcinol in conc. HCl containing 0.1% FeCl₃), heating for 20 min. at 100°, cooling, and measuring the depth of colour produced in a step photometer. The pentose solution must be diluted if its concn. exceeds 20 μ g. per c.c. Glucose, Pb⁺⁺, and NO₃⁻ (but not Ba⁺⁺) interfere. W. McC.

Determination of uronic groups in polysaccharides. A. G. NORMAN (Nature, 1939, 143, 284–285).—The rate of evolution of CO₂ with acid under standard conditions of heating etc. affords a method for detecting the presence of uronic groups. The curves indicate that these give an early max., whilst hexose material provides a longer and more regular evolution of CO₂. L. S. T.

Determination of 0.3–50 mg. of glucose by the method of Hagedorn and Jensen.—See A., 1939, III, 221.

Reaction between amines and sodium 1:2-naphthaquinone-4-sulphonate. E. G. SCHMIDT (Ind. Eng. Chem. [Anal.], 1939, 11, 99–100).—The reaction, which is the basis of Folin's colorimetric method (A., 1922, ii, 536, 540) for the determination

of the NH₂-acid content of blood, is influenced by the amount of alkali and acid added to the reaction medium. The quant. nature of the reaction is followed by comparing the colour intensities produced by interaction of aq. NH₃ and 26 different amines with that obtained from an equiv. amount of glycine. F. N. W.

Amino-acids and peptides. V. Function of iodine in amino-nitrogen analyses by the nitrous acid method. M. S. DUNN and I. PORUSH (J. Biol. Chem., 1938, 127, 261–268; cf. Kendrick and Hanke, A., 1937, III, 108).—The effect of added I⁻ on the NH₂-N vals. obtained in the analyses is explained by supposing that slightly sol. or only slightly ionised HgI₂ complexes of the NH₂-acids are produced, low results indicating production of insol. complexes. The rate of oxidation of cystine by I, as measured by production of SO₄²⁻, is much slower than that by HNO₂ in comparable concn. N₂ is produced from HNO₂ when Na₂S₂O₃ is present and hence high results are sometimes obtained. No explanation is provided of the fact that addition of KI results in a 15% decrease in the NH₂-N content of blood filtrates. W. McC.

Detection of α -amino- β -hydroxybutyric acid and its distribution in various proteins. T. HIGASHI, S. MAYEDA, and H. MATSUOKA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1939, 35, 170–173).—OH·CHMe·CH(NH₂)·CO₂H (I) is heated with Br-H₂O (and a little Br + FeSO₄) at 100° (bath) for 5–8 min., cooled, decolorised by Na₂S₂O₄, and boiled with NH₂OH·HCl for 1 min. Addition of aq. NH₃ to the cold solution affords a characteristic reddish colour (mechanism of reaction discussed). The test is sp. for (I) (apart from aspartic acid) and can be used for its detection and approx. estimation in the hydrolysis products of proteins. A. T. P.

Determination of small amounts of aspartic acid by the malic acid method of Pucher. A. A. ARHIMO (Suomen Kem., 1939, 12, B, 6).—Aspartic acid is determined by direct bromination to dibromomalic acid, oxidation of this (KMnO₄) to dibromoxalacetic acid (?), and further treatment according to Pucher (A., 1934, 1048). Tyrosine and dihydroxyphenylalanine, but not glutamic acid, can be determined in this way. M. H. M. A.

Determination of thiourea and thiocyanates. H. E. WILLIAMS (J.S.C.I., 1939, 58, 77–79).—CNS⁻ is determined by titration with Hg(NO₃)₂ in presence of dil. HNO₃ and Fe^{III} alum solution until the red colour disappears. CS(NH₂)₂ is titrated in a similar manner after adding a known vol. of standard NH₄CNS. The method can be used with N- or 0.1N-Hg(NO₃)₂, and gives results accurate to 0.02–0.035%. With mixtures containing CS(NH₂)₂ and CNS⁻, the former is eliminated by adding CdSO₄ and NaOH and boiling, and the latter determined as above. HgO or HgSO₄, but not Pb salts, can replace the CdSO₄. Determinations with the Hg(NO₃)₂ are unaffected by the presence of CO(NH₂)₂, CN·NH₂, or guanidine, but excessive amounts of dicyanodiamide interfere. Heavy metals should, in general, be absent. Chlorides lead to high

results, and when present the CNS' is first pptd. as CuCNS, or as the Cl' is removed as basic Bi chloride. In mixtures with CNS', $\text{CS}(\text{NH}_2)_2$ can be determined directly by adding aq. $\text{NaAg}(\text{CN})_2$ and NaOH , diluting, and boiling. The filtrate is titrated with AgNO_3 to a permanent opalescence (KI as indicator). The reactions occurring are $2\text{NaAg}(\text{CN})_2 + \text{CS}(\text{NH}_2)_2 + 2\text{NaOH} = \text{CN}\cdot\text{NH}_2 + \text{Ag}_2\text{S} + 4\text{NaCN} + 2\text{H}_2\text{O}$, and $4\text{NaCN} + 2\text{AgNO}_3 = 2\text{NaAg}(\text{CN})_2 + 2\text{NaNO}_3$.

L. S. T.

[Azides. IX.] *m*-Bromobenzazide as a reagent for the identification of amines. P. P. T. SAH and L. H. CHANG (Rec. trav. chim., 1939, 58, 8—11; cf. A., 1937, II, 129).—*m*-Bromobenzazide, an oil (from the hydrazide, A., 1936, 873), with the following amines etc. in PhMe at 120° yields *m*-bromophenylcarbamides (m.p. in parentheses): NH_2Ph (196—197°); *o*- (212—213°), *m*- (248—249°), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (222—223°); *p*-xylydine (227—228°); α - (259—260°) and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ (240—241°); *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$ (235—236°); *o*- (175—176°), *m*- (218—219°), and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (245—247°); *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ (236—237°); *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ (252—253°); 2 : 1 : 4- (196—190°) and 3 : 1 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ (213—214°); 1 : 3 : 4- $\text{C}_6\text{H}_3\text{MeBr}\cdot\text{NH}_2$ (237—238°); NHPh_2 (141—142°); *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (236—237°); NH_2Bz (211—212°); NH_2Ac (201—202°); NHPhAc (118—119°); *o*- (208—209°) and *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (282—283°).

E. W. W.

Determination of phenolic and naphtholic hydroxyl groups by means of benzoic anhydride. A. LEMAN (Compt. rend., 1939, 208, 357—359; cf. A., 1938, II, 274).—A phenol (0.01 mol.) or a dihydroxybenzene (0.005 mol.) with $\text{C}_6\text{H}_5\text{N}\cdot\text{Bz}_2\text{O}$ at $100^\circ/1$ hr. is benzoylated quantitatively (± 1 —2%) as shown by the titrimetric determination of BzOH obtained after hydrolysing the excess of Bz_2O .

J. L. D.

Determination of carbonyl compounds by means of 2 : 4-dinitrophenylhydrazine. H. A. IDDLIS, A. W. LOW, B. D. ROSEN, and R. T. HART (Ind. Eng. Chem. [Anal.], 1939, 11, 102—103).—The method originally devised for H_2O -sol. CO-compounds (A., 1935, 101) is extended to EtOH-sol. compounds (1). 10 c.c. of an EtOH solution of (1) are added dropwise to excess of a saturated solution of 2 : 4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ in 2*N*-HCl (II) and after dilution with 50 c.c. of (II) is kept at room temp. for 2—24 hr. The ppt. is washed with (II) and dried at 105 — 110° . The average yields obtained with the following are given in parenthesis: COPhMe (99.6), *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (97.6), $\text{CHPhBz}\cdot\text{OH}$ (99.6), mesityl oxide (93.2), benzylideneacetophenone (97.7), Bz_2 (97.7), COPh_2 (95.6), piperonal (96.5), cyclohexanone (97.3), cyclopentanone (98.6), and carvone (99.38).

F. N. W.

Condensations of furan derivatives. K. Furan derivatives analogous to chalkones. V. V. TSCHELINCEV (Bull. Soc. chim., 1939, [v], 6, 70—79; cf. A., 1932, 1140; 1933, 1179).—Ketones, $\text{CHR}\cdot\text{CH}\cdot\text{CO}\cdot\text{R}'$, give with 50—60% H_2SO_4 or conc. HCl a bright yellow colour if R is aromatic, violet or red-violet if R is furyl. Only indefinite colours are obtained with the corresponding acids or aldehydes, or

if R is aliphatic. The colours are supposed to be due to oxonium compounds resembling quinones. A. L.

Determination of aneurin. Enzymic conversion of cocarboxylase (aneurin pyrophosphate) into the free vitamin.—See A., 1939, III, 401.

Colorimetric reaction for determination of nicotinic acid. E. BANDIER and J. HALD (Biochem. J., 1939, 33, 264—271).—An aq. solution of nicotinic acid (containing 0.005—0.25 mg.) is heated at 75 — 80° for 5 min. and 1 c.c. of 4% aq. CNBr is added. After a further 5 min. heating, the solution is cooled, 10 c.c. of saturated aq. metol are added, and, after dilution to 20 c.c., the mixture is left for 1 hr. in the dark. The colour developed is then read with a Pulfrich photometer, using a S.43 filter. Solutions containing nicotinamide must first be hydrolysed. A modified technique for use with org. materials is described. Yeast contains 16—61 mg. per 100 g. dry wt.

P. G. M.

Iodometric titration of SH groups; micro-determination of cysteine and methionine in proteins. R. KUHN, L. BIRKOFER, and F. W. QUACKENBUSH (Ber., 1939, 72, [B], 407—416).—The compound is hydrolysed by boiling HI (d 1.7) containing a little KH_2PO_4 and the volatile products are conveyed by pure N_2 through an aq. suspension of red P, a solution (I) of 20% $\text{CdCl}_2 + 20\%$ BaCl_2 to retain H_2S , saturated HgCl_2 solution, and AcOH (II) containing 10% of KOAc and Br. Methionine (III) is determined in (II) by addition of HCO_2H to decolorise Br, treatment with solid KI, acidification, and titration with 0.004*N*- $\text{Na}_2\text{S}_2\text{O}_3$. (I) is treated with excess of 0.004*N*-1 and 2*N*-HCl and, after disappearance of CdS , the excess of I is determined with 0.004*N*- $\text{Na}_2\text{S}_2\text{O}_3$. For the determination of cysteine (IV) the residue in the hydrolysing flask is treated with AcOH and repeatedly evaporated to dryness at $100^\circ/\text{vac.}$ with intermediate addition of 30% AcOH until the odour of PH_3 is no longer perceptible. The residue is treated in 90% AcOH with an excess of 0.004*N*-I and after 1 min. unchanged I is determined by 0.004*N*- $\text{Na}_2\text{S}_2\text{O}_3$. The total S determined thus for casein, ovalbumin, globin, insulin, vitellin, and phalloidin is identical with that determined directly as BaSO_4 . Under the experimental conditions aneurin (V) and lactoflavin (VI) do not evolve sufficient EtI to influence the determination of (III) in proteins in the structure of which these vitamins form part. On the side of (IV), an error is not introduced by (V) but a slight correction is required for (VI). Proteins with adermin, nicotinamide, or astaxanthin as prosthetic group can be directly analysed. Immediate analysis of haemoglobins is scarcely possible, the main disturbing factor being porphyrin. The results depend so greatly on experimental conditions that a correction cannot be given. The substances to be examined for (III) must be free from OAlk and NAlk. S, present in SO_4 esters, is smoothly removed as H_2S . With sulphanilamide the total S is volatilised as H_2S whilst the basic fragments in the flask give a false val. for (IV) owing to their reducing power. The adenythiomethylpentose from yeast gives only about 66% of MeI and 33% of MeSH. Thiomethylpentose triacetate behaves similarly.

H. W.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1939.

System correlating molecular structure of organic compounds with their b.p.—See A., 1939, I, 134.

Slow oxidation of methane.—See A., 1939, I, 268.

Identification of olefines as dithiocarbimides. O. C. DERMER and G. A. DYSINGER (J. Amer. Chem. Soc., 1939, **61**, 750).— $(\text{SCN})_2$ [prep. *in situ* from NaSCN and CuSO_4 in AcOH or $\text{Pb}(\text{SCN})_2$ and Br in C_6H_6] and the appropriate olefine give ethylene-, m.p. 90–90.5°, styrene-, m.p. 102.5–103°, cyclohexene-, m.p. 58–58.5°, and 3-methylcyclohexene-dithiocarbimide, m.p. 69.5–70°. Other olefines give oils.

R. S. C.

Number of Raman frequencies of the ethylenic linking.—See A., 1939, I, 179.

Action of high-frequency coronary discharge on ethylene. J. T. EIDUS (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 737–752).—With stationary or slowly moving C_2H_4 , the high-frequency coronary discharge produces liquid (mol. wt. 450–500) and semi-solid polymerides, and the C_2H_4 simultaneously decomposes into C and H_2 . With rapidly moving C_2H_4 , 3–20% of butadiene is produced, together with C_2H_2 (an intermediate product in further reactions) and H_2 . The mechanism of these reactions is discussed.

A. LI.

Synthesis of *cis*- Δ^1 -octadecene, Δ^1 -octadecene, and octadecane- κ -diol. F. E. DEATHERAGE and H. S. OLCOTT (J. Amer. Chem. Soc., 1939, **61**, 630–631).—The Mg derivative from oleyl bromide (b.p. 160–175°/2 mm., prep. from the alcohol by $\text{PBr}_3\text{-CCl}_4$ in 65–90% yield) with 5% HCl and NH_4Cl gives crude *cis*- Δ^1 -octadecene (I), the liquid dibromide of which with Zn dust in anhyd. $n\text{-C}_8\text{H}_{17}\text{OH}$ gives excellent yields of pure (I), m.p. –2° to 0°, or with KOH in $n\text{-C}_8\text{H}_{17}\text{OH}$ at 120° yields Δ^1 -octadecene, b.p. $142^\circ \pm 2^\circ/0\text{--}45$ mm., m.p. 2–4°. Nonylloin (II) and $\text{H}_2\text{-PtO}_2$ in abs. EtOH give octadecane- κ -diol, β -, m.p. 127°, and α -form, impure; the derived dibromide did not yield (I); 3% Na-Hg and abs. EtOH convert (II) into octadecan-1-one, m.p. 47°.

R. S. C.

Sodium ethylene carbide. O. C. DERMER and C. LATHROP (J. Amer. Chem. Soc., 1939, **61**, 750–751).—Walker's compound (A., 1927, 837) is not formed from pure C_2H_4 , and pure C_2H_4 is unaffected by Na at 150°.

R. S. C.

Establishment of structure of hydrocarbons of the $\text{C}_n\text{H}_{2n-2}$ series. M. D. BONI (Sci. Mem. State Univ. Leningrad, Chem. Ser., 1938, No. 18, 3–37).—Reactions depending on addition of halogen acids or

OH -acids to $\text{C}\equiv\text{C}$ or $\text{C}:\text{C}:\text{C}$ cannot serve for the establishment of the structure of such hydrocarbons, owing to the large no. of isomeric products obtained. Allene hydrocarbons are oxidised by KMnO_4 or $\text{Mg}(\text{MnO}_4)_2$ as follows: $\text{CRR}'\text{:C:CHR}''$ (I) + O + $\text{H}_2\text{O} \rightarrow \text{CRR}'\text{:C(OH):CHR}''\text{:OH} \rightarrow \text{CHRR}'\text{:CO:CHR}''\text{:OH}$ (+ O) $\rightarrow \text{CHRR}'\text{:CO}_2\text{H} + \text{R}''\text{:CO}_2\text{H}$ ($\text{R} = \text{R}' = \text{R}'' = \text{H}$ or Me ; $\text{R} = \text{R}' = \text{Me}$, $\text{R}'' = \text{H}$). Identification of the reaction products cannot serve for differentiating allene from isomeric C_2H_2 hydrocarbons, which give the same products. Ozonolysis proceeds as follows: (I) + $2\text{O}_3 \rightarrow$ diozonide (+ H_2O) $\rightarrow \text{CORR}' + \text{R}''\text{:CO}_2\text{H} + \text{CO}_2$; identification of the reaction products in this case allows the establishment of the structure of the hydrocarbon.

R. T.

Polymerisation of dideuteroacetylene. G. R. CLEMO and A. C. ROBSON (J.C.S., 1939, 429–430).—The yield of solid and liquid condensation products (70%) is > doubled (cf. A., 1935, 967) by discontinuous working and dispensing with the carrier gas. Besides C_6D_8 (yield unchanged) (new m.p. 6.2–6.5°; cf. Ingold *et al.*, A., 1936, 1322), the following were isolated: octadeuterotoluene, b.p. 105–120° [α 2 : 4. (NO_2)₂-derivative, m.p. 65–66°]; octadeuteroindene, b.p. 175–190°, characterised as hexadeutero-1-(α -hydroxybenzyl)-3-benzylideneindene, m.p. 136°; C_{10}D_8 ; decadeuterofluorene, m.p. 115–117° (picrate, m.p. 81–83°), oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to octadeuterofluorenone, m.p. 84°; decadeuteroptyrene, m.p. 148–149° (picrate, m.p. 217–219°).

S. H. H.

Alkylacetylenes and their derivatives. XXX. Preparation of α -alkyl- β -alkenylacetylenes. W. F. ANZILOTTI and R. R. VOGT (J. Amer. Chem. Soc., 1939, **61**, 572–573; cf. A., 1939, II, 46).— $\text{CH}_2\text{Br-CHBr-OEt}$ and $\text{CH}_3\text{C-MgAlk}$ in Et_2O give ethers, $\text{CH}_2\text{Br-CH(OEt)-C:Alk}$, which decompose when distilled, but, when boiled with Zn dust in 90% EtOH , give 70–77% of hept-, b.p. 44.3–44.7°/75 mm., oct-, b.p. 61.5–62°/60 mm., non-, b.p. 27.7–28.2°/4 mm., dec-, b.p. 45–45.4°/4 mm., and dodec-, b.p. 77.5–78°/4 mm., Δ^2 -*en*- Δ^2 -inene. CHMeBr-CHBr-OEt yields similarly non-, b.p. 70–70.5°/29 mm., and dec-, b.p. 54.5–55°/5 mm., Δ^2 -*en*- Δ^2 -inene.

R. S. C.

Derivatives of vinylacetylene. General survey. I. N. NAZAROV. I. Esters of vinyl- and isopropenyl-propionic acid. I. N. NAZAROV and M. V. KUVARZINA. II. Condensation of vinyl- and isopropenyl-acetylene with ketones to give vinylacetylenylcarbinols. III. Esterification and dehydration of vinylacetylenylcarbinols. Acet-

ates of vinylacetylenylcarbinols and homologues of divinylacetylenes. IV. Ethers of vinylacetylenylcarbinols. V. β -Alkoxyethyl ethers of vinylacetylenylcarbinols. VI. Hydrolysis and alcoholysis of vinylacetylenylcarbinol ethers. I. N. NAZAROV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 671—676, 677—682, 683—694, 695—705, 706—718, 719—725, 726—736).—I. *Me*, b.p. 71°/40 mm., *Et*, b.p. 65°/10 mm., and *isoamyl vinylpropionate*, b.p. 106—108°/20 mm. (from $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$), and *Me*, b.p. 66°/18 mm., *Et*, b.p. 82.5—83°/20 mm., and *isoamyl isopropenylpropionate*, b.p. 108—110°/14 mm. (from $\text{CH}_2\text{:CMe}\cdot\text{C}\cdot\text{CH}$), all polymerise spontaneously, with absorption of O_2 , to solid rosin-like polymerides.

II. Vinyl- and isopropenyl-acetylene condense (KOH) almost quantitatively with aliphatic and alicyclic ketones to give polymerisable *tert.* alcohols: *dimethyl-* (I), b.p. 58—59°/13 mm., *methylethyl-* (II), b.p. 64—65°/10 mm., *methyl-n-propyl-*, b.p. 70—71°/7 mm., and *methyl-*tert.*-butyl-vinylacetylenylcarbinol* (III), b.p. 70—70.5°/8 mm., *1-vinylacetylenyl-cyclohexanol* (IV), b.p. 102—103°/10 mm., *-4-methyl-* (V), b.p. 100—102°/7 mm., and *-2-methyl-cyclohexanol*, b.p. 92—93°/5 mm., and the corresponding *isopropenylacetylenyl* compounds (except the *-2-methyl-cyclohexanol*), having respectively b.p. 58—58.5°/8 mm., 65—66°/8 mm., 75—77°/6 mm., 77°/7 mm., m.p. 57—58°, and m.p. 51—52°.

III. (I) with Ac_2O at 0—10° yields the *acetate*, b.p. 59—60°/7 mm., with a little *di-(α -vinylacetylenyl-isopropyl) ether*, b.p. 100—101°/7 mm.; with Ac_2O and a trace of conc. H_2SO_4 at 60—70°, or with 60% H_2SO_4 at 50—60°, it is dehydrated to $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{C}\cdot\text{CMe}\cdot\text{CH}_2$, and with HCl yields the *chloride*, b.p. 31—32°/10 mm., which does not polymerise. Similarly (II) yields an *acetate*, b.p. 66—67°/6 mm., and a dehydration product, C_8H_{10} , b.p. 22—23°/8 mm., and (III) an *acetate*, b.p. 83—84°/8 mm., and dehydration product, $\text{C}_{10}\text{H}_{14}$, b.p. 46—47°/14 mm.; (IV) and (V) yield the *acetates*, b.p. 103—104.5°/7 mm. and 109—109.5°/7 mm., and Δ^1 -cyclohexenes, b.p. 88—90°/15 mm. and 96.5—97°/12 mm., respectively; *dimethyl-*, and *methyl-ethyl-*, *-n-propyl-*, and *-tert.-butyl-isopropenylacetylenylcarbinols* yield *acetates*, b.p. 61—62°/6 mm., 69—71°/6 mm., 82—83°/6 mm., and 83.5°/6 mm. respectively, whilst the last two carbinols give dehydration products, $\text{C}_{10}\text{H}_{14}$ (? $\text{CH}_2\text{:CMe}\cdot\text{C}\cdot\text{C}\cdot\text{CMe}\cdot\text{CHEt}$), b.p. 60—62°/17 mm., and $\text{C}_{11}\text{H}_{16}$, b.p. 48°/8 mm. *Dimethylacetylenylcarbinol acetate* has b.p. 133—133.5°.

IV. *tert.*-Vinylacetylenylcarbinols with monohydric alcohols in presence of H_2SO_4 yield ethers which polymerise (to transparent gels) more slowly than the carbinols; with $(\text{CH}_2\text{:OH})_2$ they give β -hydroxyethyl ethers, which polymerise as rapidly as the carbinols, together with traces of the glycol di-ethers. The following are the b.p. of the ethers of (I): *Me*, 29—30°/8 mm., *Et*, 36—37°/8 mm., *Pr*, 55—56°/11 mm., *Pr ^{β}* , 40—41°/9 mm., *allyl*, 54°/9 mm., *Bu*, 66—67°/9 mm., *Bu ^{β}* , 55—56°/7 mm., *isoamyl*, 68—69°/7 mm., *benzyl*, 96—97°/2 mm., β -hydroxyethyl, 88—89°/7 mm. (*acetate*, b.p. 112—114°/15 mm.), *ethylene glycol di-ether*, 127—129°/8 mm.; of (II): *Me*, 42—43°/10 mm., *Et*, 50—51.5°/10 mm., *Bu*, 96—97°/24 mm., *isoamyl*, 95—96°/16 mm., β -hydroxyethyl, 116—117°/21

mm.; and of (V): β -hydroxyethyl, 140—143°/10 mm. (*acetate*, b.p. 150—151°/9 mm.).

V. *tert.*-Vinylacetylenylcarbinols with monoalkyl ethers of $(\text{CH}_2\text{:OH})_2$ in presence of H_2SO_4 yield readily polymerisable β -alkoxyethyl ethers having the following b.p.: from (I): *Me*, 78—80°/10 mm., *Et*, 88—90°/11 mm., *Pr*, 100—101°/11 mm., *Bu*, 99—100°/5.5 mm., β -methoxy- β -ethoxyethyl, 115—117°/7 mm.; and from (II): *Me*, 78—80°/6 mm., *Et*, 87—89°/6 mm., *Pr*, 100—102°/6 mm., β -methoxy- β -ethoxyethyl, 106—107°/2 mm.

VI. Ethers of *tert.*-vinylacetylenylcarbinols give with 10% H_2SO_4 the original alcohols, and with conc. or gaseous HCl the *tert.* chlorides, which can be hydrolysed to the alcohols. Treatment of the ethers with alcohols containing conc. H_2SO_4 gives ethers of the new alcohols. All these reactions are reversible.

A. LI.

Aliphatic chloro-derivatives. XIII. Action of chlorine on *as*-methylethylethylene. R. GUTNER and D. TISCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 1062—1067).— $\text{CH}_2\text{:CMeEt}$ and Cl_2 at 5—8° yield chiefly *tert.*- $\text{C}_5\text{H}_{11}\text{Cl}$, with $\text{CHMeCl}\cdot\text{CMe}_2\text{Cl}$; in presence of NaHCO_3 the products are $\text{CH}_2\text{:CMe}\cdot\text{CHMeCl}$, $\text{CH}_2\text{:CEt}\cdot\text{CH}_2\text{Cl}$, and $\text{CHMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Cl}$. R. T.

Radioactive organic bromo-compounds. E. FRIEDMANN, A. K. SOLOMON, and N. T. WERTHESSEN (Nature, 1939, 143, 472).—Experiments giving the relative amounts of radioactive ^{82}Br introduced into org. compounds by means of (a) Sandmeyer's reaction, and (b) addition of Br to a double linking, are described. Method (b) yields a higher concn. of radioactive material. L. S. T.

Esterification of alcohols. D. N. VASKEVITSCH and T. F. BULANOVA (J. Gen. Chem. Russ., 1938, 8, 1091—1097).—A 7:2 Cu-MnO catalyst, activated with Ag, is reduced by passing EtOH at 300°, to afford an active and stable catalyst of the reaction $\text{R}\cdot\text{CH}_2\text{:OH} + \text{R}'\cdot\text{OH} \rightarrow \text{R}\cdot\text{CO}_2\text{R}' + \text{H}_2$, at 270—280° ($\text{R} = \text{H}$, $\text{R}' = \text{Bu}^\beta$; $\text{R} = \text{H}$, $\text{R}' = \text{iso-C}_5\text{H}_{11}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Bu}^\beta$; $\text{R} = \text{Me}$, $\text{R}' = \text{iso-C}_5\text{H}_{11}$; $\text{R} = \text{Pr}^\beta$, $\text{R}' = \text{iso-C}_5\text{H}_{11}$). R. T.

Selective catalysis. III. Influence of solvents on selective hydrogenation of unsaturated compounds. I. F. BOGDANOV and E. I. BASCHKIROVA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 529—537).—The rates of hydrogenation of allyl alcohol and of crotonic acid (Pt) are approx. equal and in H_2O are one quarter of those in EtOH or AcOH ; with mixtures the former is hydrogenated first in all three solvents. S. H. H.

Preparation of α -substituted β -ethylenic alcohols. O. K. HOVO (Compt. rend., 1939, 208, 528—530).—Mg crotyl bromide with MeCHO , EtCHO , and $\text{CH}_2\text{:CH}\cdot\text{CHO}$ in Et_2O yields δ -hydroxy- γ -methyl- Δ^1 -pentene, b.p. 125—126°, Δ^1 -hexene, b.p. 140—141°, and Δ^1 -hexadiene, b.p. 55—56°/14 mm., respectively, the structures of which are supported by Raman spectra measurements. In each reaction dicrotyl condensation products (cf. A., 1935, 728) are formed. The reactions are explained on an electronic basis. J. L. D.

Application of Tschugaev's xanthate method of preparing unsaturated hydrocarbons to dihydric alcohols. A. F. KOSTERNAJA (Sci. Mem. State Univ. Leningrad, Chem. Ser., 1938, No. 18, 127—156).— $(\text{ONa}\cdot\text{CH}_2)_2$ and CS_2 in Et_2O are heated at $40\text{--}45^\circ$ (4—8 hr.), the insol. residue is dried over H_2SO_4 , and boiled with MeI in EtOH , to yield *dithioglycol di(methyltrithiocarbonate)*, $(\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}_2\text{Me})_2$, m.p. $57\text{--}58^\circ$. Glycol diethylidixanthate distilled at 195° yields C_2H_2 , COS , and EtSH . $\text{CH}_2\text{Br}\cdot\text{CHMeBr}$ or $(\text{CHMeBr})_2$ and $\text{OEt}\cdot\text{CS}_2\text{Na}$ in EtOH heated at 70° for 5—7 hr. yield methyl- or $\alpha\beta$ -dimethyl-glycol diethylidixanthate, which when distilled at 195° yield CH_3CMe or divinyl, together with COS and EtSH . R. T.

Action of anhydrous oxalic acid on polyhydric alcohols and hydrocarbons. A. G. EVDOKIMOV (Sci. Mem. State Univ. Leningrad, Chem. Ser., 1938, No. 18, 38—100).—Anhyd. $\text{H}_2\text{C}_2\text{O}_4$ and glycol heated at 100° for 2 hr. yield H_2O , CO_2 , HCO_2H , and glycol mono- (I) and di-formate. (I) at $240\text{--}260^\circ$ yields CO , CO_2 , $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$, and resins; it decomposes probably as follows: $(\text{I}) \rightarrow \text{HCO}_2\text{H} + \text{MeCHO}$, and these yield secondary decomp. and condensation products. $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ and $\text{H}_2\text{C}_2\text{O}_4$ similarly yield H_2O , CO_2 , and α -formoxypropan- β -ol, b.p. $177\text{--}177.5^\circ$, decomp. at 260° to give CO , CO_2 , EtCHO , COMe_2 , Δ^8 -propen- β -al, and resins. $(\text{OH}\cdot\text{CHMe})_2$ and $\text{H}_2\text{C}_2\text{O}_4$ give H_2O , CO_2 , HCO_2H , and β -formoxybutan- γ -ol, b.p. $174\text{--}176^\circ$, decomp. at 260° , with production of H_2O , CO , CO_2 , $(\text{CHMe})_2$, COMeEt , and HCO_2H . $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ and $\text{H}_2\text{C}_2\text{O}_4$ afford H_2O , CO_2 , HCO_2H , and Pr^iCHO , mannitol gives CO , CO_2 , HCO_2H , $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$, a compound, $\text{C}_6\text{H}_{10}\text{O}_3$, b.p. $156.5\text{--}158^\circ/17\text{ mm.}$, and tarry matter, arabinose gives CO_2 , H_2O , furfuraldehyde, HCO_2H , and humins, and other carbohydrates (fructose, glucose, starch, cellulose) yield CO_2 , H_2O , $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, HCO_2H , and humins. R. T.

Pentaerythritol monobromo- and monoiodohydrins. F. GOVAERT and M. BEYAERT (Natuurwetensch. Tijds., 1939, 21, 29—31).—Pentaerythritol monobromohydrin, m.p. 76° , and monoiodohydrin, m.p. 106° , have been obtained by fractional distillation in a high vac. (1 mm.) of the mother-liquors from the prep. of the dihalogenohydrins. S. C.

Etherification of isoamyl alcohol. (SIGNA.) L. RAFFA (Gazzetta, 1939, 69, 14—18).— $(\text{iso-C}_5\text{H}_{11})_2\text{O}$ can be prepared from $\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$ (I) and conc. H_2SO_4 (II) under pressure (cf. Oddo, "Trattato di Chimica organica," 1930), best from (I) + 10 wt.-% of (II), at $145\text{--}150^\circ$ for 12 hr. E. W. W.

Synthesis of $\beta\beta'$ -dichloro- and β' -chloro- β -hydroxy-ethers. Reaction of ethylene chlorohydrin and glycol with benzenesulphondichloroamide, in presence of olefines. M. V. LICHOSCHERSTOV, V. E. SHABOTINSKAJA, and L. D. PAVLOVSKAJA (J. Gen. Chem. Russ., 1938, 8, 997—1007).—The general reactions $\text{PhSO}_2\cdot\text{NCl}_2 + \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OCl}$ (I) + $\text{PhSO}_2\cdot\text{NHCl}$ (II); $(\text{I}) + >\text{C}:\text{C}< + (\text{II}) \rightarrow >\text{CCl}\cdot\dot{\text{C}}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} + >\text{CCl}\cdot\dot{\text{C}}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ are described, and the following ethers are so prepared: β -chloroethyl β' -chloro- α' -m* (A, II.)

methylpropyl, b.p. $193\text{--}194^\circ$, from $(\text{CHMe})_2$, α' -chloromethylpropyl, b.p. 195.5° , from $\text{CH}_2\cdot\text{CHEt}$, and α' -chloromethyl- α' -methylethyl ether, b.p. 192° , from $\text{CH}_2\cdot\text{CMe}_2$, $(\text{CHMe})_2$ and $(\text{CH}_2\cdot\text{OH})_2$ in CHCl_3 and $\text{PhSO}_2\cdot\text{NCl}_2$ yield β -hydroxyethyl β' -chloro- α' -methylpropyl ether (III), b.p. $74\text{--}75^\circ/2\text{ mm.}$, together with glycol $\beta\beta'$ -dichloro- $\alpha\alpha'$ -dimethylpropyl ether, b.p. $103\text{--}105^\circ/3\text{ mm.}$ (III) and KOH at $130\text{--}135^\circ$ yield 1:2-dimethyldioxan. R. T.

Action of Raney nickel on organic sulphur compounds. J. BOUGAULT, E. CATTELAINE, and P. CHABRIER (Compt. rend., 1939, 208, 657—659).—Many org. S compounds in H_2O or EtOH at room temp. lose S when shaken with Raney Ni. Ni_2S and H_2 are obtained in each case. The following react (reaction products in parenthesis): CS_2 (CH_4); $\text{CS}(\text{NH}_2)_2$ (CH_4 , NH_3 , NH_2Me); $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$ (NH_3 , NH_2Me , PhMe); $\text{SH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ (NHPhAc); $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (AcOH); $(\text{CH}_2\cdot\text{SH})_2$ (C_2H_6); $\text{CHPh}\cdot\text{C}(\text{SH})\cdot\text{CO}_2\text{H}$ ($\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$); AcSH (in H_2O , AcOH ; in EtOH , MeCHO); 6-hydroxy-2-thiol-5-benzyl-1:3:4-triazine (I) [2:6-dihydroxy-5-benzyl-1:3:4-triazine (II)]; S-benzyl ether of (I) [(II) and PhMe]. J. L. D.

Higher n-aliphatic acids and their methyl and ethyl esters. F. FRANCIS and S. H. PIPER (J. Amer. Chem. Soc., 1939, 61, 577—581).—F.p., m.p., resolidification temp., and crystal spacings of pure acids, $\text{C}_n\text{H}_{2n+1}\cdot\text{CO}_2\text{H}$ (even no. of C, $n = 11\text{--}45$; odd no. of C, $n = 16\text{--}24$ and 28), and their Me and Et esters are reported. Dimorphism of the esters is discussed. R. S. C.

[Attempted] synthesis of irone. B. A. KILBY and F. B. KIPPING (J.C.S., 1939, 435—439).— $(\text{CH}_2\cdot\text{CMe})_2$ (prep. in 70% yield from pure pinacol) and pure HBr give a bromide, isomerised, when kept, to $\text{CMe}_2\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ (95% yield), b.p. $49\text{--}52^\circ/15\text{ mm.}$, which with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ gives Et α -acetyl- $\gamma\delta$ -dimethyl- Δ^8 -hexenoate, b.p. $127\text{--}130^\circ/11\text{ mm.}$ Hydrolysis by cold, 10% aq. KOH then gives $\beta\gamma$ -dimethyl Δ^8 -hepten- ζ -one, b.p. 188° (semicarbazone, m.p. 160°), converted by O_3 into $(\text{COMe}\cdot\text{CH}_2)_2$ and COMe_2 (and its peroxide), and by Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in not too much C_6H_6 into Et β -hydroxy- ε -methyl- $\alpha\beta$ -dihydrogeranate [β -hydroxy- $\beta\zeta$ -trimethyl- Δ^8 -octenoate] (I), b.p. $146\text{--}148^\circ/15\text{ mm.}$ Dehydration of this ester to ε -methylgeranic acid could not be effected; at 200° EtOAc and $\text{CMe}_2\cdot\text{CMe}\cdot[\text{CH}_2]_2\cdot\text{COMe}$ (II) are formed; $\text{BzCl}\cdot\text{NaOH}$ and $\text{AcCl}\cdot\text{NaOAc}$ have no effect; ZnCl_2 gives tars; I, $\text{P}_2\text{O}_5\text{--C}_6\text{H}_6$, or, much less well, $\text{PBr}_3\text{--C}_5\text{H}_5\text{N}$, HBr , etc., gives Et 2:2:3:6-tetramethyltetrahydropyran-6-acetate (III), b.p. $121\text{--}122^\circ/14\text{ mm.}$ 10% $\text{KOH}\text{--EtOH}$ hydrolyses (I) to the corresponding acid, b.p. $168^\circ/15\text{ mm.}$, unchanged by $\text{Ac}_2\text{O}\text{--NaOAc}$, decomposed by P_2O_5 or by distilling its Ba salt with $(\text{HCO}_2)_2\text{Ba}$ and sand at 0.4 mm. into (II) and AcOH , and converted by P_2O_5 in cold C_6H_6 into the acid, b.p. $110\text{--}116^\circ/0.05\text{ mm.}$, corresponding with (III). Et β -hydroxy- $\alpha\beta$ -dihydrogeranate, b.p. $134\text{--}138^\circ/12\text{--}13\text{ mm.}$, is similarly prepared from methylheptenone, and with hot $\text{P}_2\text{O}_5\text{--C}_6\text{H}_6$ gives Et 2:2:6-trimethyltetrahydropyran-6-acetate, b.p. $118^\circ/13\text{ mm.}$ Addition of K in *tert.*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ and (II) in Et_2O to Et_2O

saturated with C_2H_2 at -15° and then of more C_2H_2 at 0° gives *dehydromethyl-linalool* [γ -hydroxy- γ - γ -trimethyloct- Δ^1 -en- Δ^a -inene] (IV), b.p. $97-99^\circ/10$ mm., which with HCO_2H-H_2O gives 2:2:3:6-tetramethyl-6-acetylenyltetrahydropyran, b.p. $64-66^\circ/10$ mm. (absorbs 2 H_2). In AcOH in presence of PtO_2 (IV) absorbs 3 H_2 , but in presence of $Pd-CaCO_3$ in EtOH hydrogenation can be regulated so as to give methyl-linalool (V), b.p. $98-102^\circ/10$ mm., dihydromethyl-linalool, b.p. $99-102^\circ/10$ mm., or the H_6 -derivative. Attempts to convert (V) into methylgeraniol (VI) by $CCl_3-CO_2H-AcOH$ gave 2:2:3:6-tetramethyl-6-vinyltetrahydropyran, b.p. $76-78^\circ/14$ mm., and other products; PBr_3 and a little C_3H_5N in light petroleum convert (V) into the *bromide*, b.p. $116-118^\circ/10$ mm., and thence (by $NaOAc$) into a pyran, b.p. $73-74^\circ/13$ mm., (by $AgOBz$) into a benzoate, b.p. $140-142^\circ/0.35$ mm., hydrolysed ($KOH-MeOH$) to a substance, b.p. $114-130^\circ/13$ mm. [not (VI)]. R. S. C.

Properties of bivalent metal oleates. I. S. S. BHATNAGAR, P. L. KAPUR, and A. HUSSAIN (Proc. Indian Acad. Sci., 1939, 9, A, 143-158).—Zn and Mg oleates have been prepared from Na oleate and the appropriate sulphate under various conditions. The ratio Zn or Mg to acid is never strictly stoichiometric. When Zn oleate is prepared by refluxing Zn dust and oleic acid the ratio of Zn to acid is 1.00:2.00 and the oleate has a considerably higher m.p. and lower solubility in C_6H_6 . From measurements (on C_6H_6 solutions) of solubility, mol. complexity, η , surface tension, interfacial tension, conductivity, and mol. magnetic rotation it is shown that variations are most probably due to adsorption of various ions by the metal soaps, that the behaviour of Zn oleate is that of a gel, and that Mg oleate behaves more like a colloidal electrolyte. W. R. A.

Cerebronic and nervonic acid. A. MÜLLER [with I. BINZER] (Ber., 1939, 72, [B], 615-619).—Et erucate is reduced by Na and amyl alcohol to erucyl alcohol, m.p. 34° , which with PBr_3 in PhMe at $>5^\circ$ gave α -bromo- Δ^7 -docosene, b.p. $135-150^\circ$ (bath)/high vac., incipient solidifying temp. $\sim 8^\circ$ (probably a mixture of stereoisomerides). This with $CHNa(CO_2Et)_2$ affords *Et₂ docosylenemalonate*, b.p. $175-220^\circ$ (bath)/high vac., which is hydrolysed and decarboxylated to the stereoisomeric *tetracosenoic acids*, m.p. $70-6^\circ$ (corr.) and 41.1° (corr.) respectively, reduced (Ni at 180°) to *tetracosanoic acid* (I), m.p. 84.0° . Gradual addition of Br to (I) and red P at 100° yields α -bromotetracosanoic acid, m.p. 74° or, after resolidification, m.p. 75.2° , which with aq. KOH affords *di- α -hydroxytetracosanoic acid*, m.p. 99.7° . This is resolved by strychnine in warm $CHCl_3$ into the *l-acid* (II), m.p. 99° , $[\alpha]_D^{25} -3.13^\circ$ in anethole (*strychnine salt*), and non-homogeneous *d-acid*. The solubility of (II) in C_5H_5N is distinctly $<$ that of the natural cerebronic acid. The homogeneity of natural nervonic acid appears doubtful but it probably consists mainly of *cis-n- Δ^5 -tetracosenoic acid*. Addition of Br to this acid affords β -dibromotetracosanoic acid, which with red P and Br affords $\alpha\beta$ -tribromotetracosanoic acid; this is transformed by an excess of NaI in boiling $COMe_2$ into α -iodo- Δ^5 -tetracosenoic acid,

which with $KOH-EtOH-H_2O$ at 100° yields α -hydroxy- Δ^5 -tetracosenoic acid. H. W.

Keto-enol tautomerism of pyruvate ion.—See A., 1939, I, 268.

Interchange between chromioxalate ion and oxalate ion, using radio-carbon.—See A., 1939, I, 274.

Preparation of *tert*-butylmalonic acid and its derivatives. M. T. BUSH (J. Amer. Chem. Soc., 1939, 61, 637-638).—Addition of $CH_3Bu^tCO_2H$ (I) in light petroleum (II) to Na in C_6H_6 , and then of $n-C_5H_{11}Cl$ and more (II), and finally of CO_2 at $44-63^\circ$, gives 45% of $CHBu^t(CO_2H)_2$, m.p. $155-157^\circ$ [at $170-180^\circ$ gives (I); *di(ethylamide)*, m.p. $151.3-151.7^\circ$ (corr.)], converted into *tert*-butylbarbituric acid, m.p. $235.5-236.8^\circ$ (corr.) (lit. $230-231^\circ$), which is physiologically inactive. R. S. C.

Optically active acid anhydrides. III. Optically active anhydrides of alkylated succinic and glutaric acids. E. BERNER and R. LEONARDESEN [with, in part, A. T. GRENTOF and K. DAHL] (Annalen, 1939, 538, 1-43).—There appears to be no regularity in the direction on magnitude of the change in optical activity on passing from the acids to the anhydrides or esters. The principle of optical superposition applies to the anhydrides of the dialkylated succinic acids but not to the acids or esters. *r*-Methylsuccinic acid, which is shown to be a true racemate, is resolved into its optical antipodes by fractional crystallisation of the strychnine H salt. *d*-Methylsuccinic acid has m.p. 115° , $[\alpha]_D^{25} +10.44^\circ$ in H_2O for $\sim 20\%$ solution. Other vals. in H_2O and in EtOH are recorded. The true $[\alpha]_D$ is calc. to be $\pm 14.92^\circ$. Measurement of the $[\alpha]_D^{25}$ of the Na H and Na_2 salts give the vals. $+14.50^\circ$, and $+3.91^\circ$ for the primary and *sec.* ions. *Me₂ d-methylsuccinate*, from the acid and CH_3N_3 in Et_2O , has b.p. $80-81^\circ/12$ mm., $[\alpha]_D^{25} +6.44^\circ$ in substance, $[\alpha]_D^{25} +4.40^\circ$ in EtOH (85.93 g. in 100 g. of solution; other vals. quoted). The acid is transformed by $SOCl_2$ into *d-methylsuccinic anhydride*, m.p. 69.5° , $[\alpha]_D^{25} +32.6^\circ$ in dioxan; the alterations of the vals. of $[\alpha]_D$ are recorded for solutions of the anhydride in H_2O and EtOH. It can be distilled without becoming racemised. Its optical activity in the molten, undercooled condition has been observed. The crude *laevo*-acid as obtained from the mother-liquors of the resolution is best converted by $AcCl$ into the anhydride, which can be purified by crystallisation from C_6H_6 ; the *l-anhydride* has m.p. $69-70^\circ$ and the *l-acid*, m.p. 115° , $[\alpha]_D^{25} -9.87^\circ$ (*d-acid* $+9.98^\circ$ under the same conditions). *r*-Ethylsuccinic acid can be resolved into its optical antipodes by repeated crystallisation of the strychnine salt from H_2O . It appears preferable to follow the resolution only so far that the active components have $[\alpha] \leq 13^\circ$. They are then converted into their anhydrides, which are purified by distillation. After some time at 0° the distillates separate crystals of the active anhydrides, which are separated by pressing from the liquid, inactive material and further purified by pptn. from Et_2O by light petroleum. They are hydrated by H_2O . *d*-Ethylsuccinic acid has m.p. 96° , $[\alpha]_D^{25} +18.4^\circ$ in H_2O , $+26.0^\circ$ in $COMe_2$.

whilst the *l*-acid has m.p. 96° , $[\alpha]_D^{20} -18.5^\circ$ in H_2O . The true $[\alpha]_D^{20}$ is $\pm 18.13^\circ$ whilst the vals. for the primary and sec. ion are $[\alpha]_D^{20} +21.19^\circ$ and -1.78° respectively. *Me*₂ *l*-ethylsuccinate has b.p. $91-94^\circ/13$ mm., $[\alpha]_D^{20} -14.89^\circ$. *d*-Ethylsuccinic anhydride has m.p. 32.5° , $[\alpha]_D^{20} -9.75^\circ$ (undercooled), $[\alpha]_D^{20} +0.3^\circ$ in H_2O (extrapolated), whereas *l*-ethylsuccinic anhydride has m.p. 32.5° , $[\alpha]_D^{20} -0.1^\circ$ in H_2O (extrapolated). *r*- α -Dimethylsuccinic acid is resolved into its optical antipodes by successive use of brucine and strychnine. The *d*-acid has m.p. $134-135^\circ$, $[\alpha]_D^{20} +8.02^\circ$ in H_2O ($p = 4.157$), and the *l*-acid m.p. $134-135^\circ$, $[\alpha]_D^{20} -8.04^\circ$ in H_2O ($p = 5.053$), -5.77° in EtOH ($p = 7.978$), other vals. being recorded. For the primary and sec. ions of the *l*-acid the vals. $[\alpha]_D^{20} -43.6^\circ$ and $+5.25^\circ$ are quoted. *Me*₂ *d*- α '-dimethylsuccinate has b.p. $104^\circ/27$ mm., $[\alpha]_D^{20} -9.32^\circ$ in substance. *d*- α '-Dimethylsuccinic anhydride has m.p. 107° , $[\alpha]_D^{20} +116.3^\circ$ in C_6H_6 , $+8.5^\circ$ in dioxan. *d*- α '-Diethylsuccinic acid, m.p. 126° , $[\alpha]_D^{20} +42.04^\circ$ in H_2O ($p = 2.623$), $+26.14^\circ$ in EtOH ($p = 3.742$), $+28.9^\circ$ in $COMe$, is isolated by repeated treatment of the *r*-acid with strychnine in H_2O . For the primary and sec. ion the vals. $[\alpha]_D^{20} +53.26^\circ$ and $+1.57^\circ$ in H_2O are given. *Me*₂ *l*- α '-diethylsuccinate has b.p. $104^\circ/13$ mm., $[\alpha]_D^{20} -17.41^\circ$ in substance. Slight racemisation is considered to occur during the formation of *d*- α '-diethylsuccinic anhydride, b.p. $108-109^\circ/11$ mm., $[\alpha]_D^{20} +47.11^\circ$ in substance. α -Methyl- α '-ethylsuccinic acid, m.p. 106° , is readily resolved into its optical antipodes by crystallisation of the strychnine H salt from H_2O . It appears to consist of pseudoracemic crystals. *d*- α -Methyl- α '-ethylsuccinic acid has m.p. 180° , $[\alpha]_D^{20} +5.11^\circ$ in H_2O , $+7.97^\circ$ in EtOH ($p = 7.645$), $+6.56^\circ$ in dioxan ($p = 8.584$). The true $[\alpha]_D^{20}$ is $+3.11^\circ$. The primary and sec. ions have $[\alpha]_D^{20} +3.53^\circ$ and -2.23° in H_2O respectively. *Me*₂ *d*- α -methyl- α '-ethylsuccinate has b.p. $97^\circ/18$ mm., $[\alpha]_D^{20} +8.01^\circ$ in substance. The conversion of the acid by $SOCl_2$ into *d*- α -methyl- α '-ethylsuccinic anhydride, b.p. $118-119^\circ/12$ mm., $[\alpha]_D^{20} -11.72^\circ$ in substance, occurs without racemisation. The resolution of the isomeric *r*- α -methyl- α '-ethylsuccinic acid of lower m.p. is more difficult and is best effected by strychnine or brucine in water. The *d*-acid has m.p. 81° , $[\alpha]_D^{20} +25.69^\circ$ in H_2O ($p = 4.832$), $+13.55^\circ$ in EtOH ($p = 5.263$), whilst for the primary and sec. ions the vals. $[\alpha]_D^{20} \sim -54.7^\circ$ and $\sim +7.50^\circ$ in H_2O are quoted. The *Me*₂ ester of the *l*-acid has b.p. $97-98^\circ/14$ mm., $[\alpha]_D^{20} -2.54^\circ$. The corresponding *d*- α -methyl- α '-ethylsuccinic anhydride has b.p. $114-115^\circ/15$ mm., $[\alpha]_D^{20} +62.02^\circ$. Treatment of α -methylglutaric acid, which is a true racemate, with strychnine in H_2O leads to the isolation of *d*-methylglutaric acid, $[\alpha]_D^{20} +20.04^\circ$ in H_2O ($p = 7.280$), $+21.74^\circ$ in EtOH ($p = 5.268$), true $[\alpha]_D^{20} +22.1^\circ$. The primary and sec. ions have $[\alpha]_D^{20} +13.5^\circ$ and $+1.8^\circ$ in H_2O respectively. *Me*₂ *d*- α -methylglutarate has b.p. $91-91.5^\circ/9$ mm., $[\alpha]_D^{20} +24.46^\circ$. *d*- α -Methylglutaric anhydride, m.p. 56.5° , $[\alpha]_D^{20} -38.8^\circ$ in H_2O (extrapolated), $[\alpha]_D^{20} +44.35^\circ$ (undercooled), is described. *r*- α -Methylglutaric anhydride has m.p. $35-36^\circ$. *r*- α -Ethylglutaric acid is resolved into its optical antipodes by crystallisation of the normal strychnine salt

from H_2O . *d*- α -Ethylglutaric acid has m.p. 42° , $[\alpha]_D^{20} +16.51^\circ$ (homogeneous; undercooled), $[\alpha]_D^{20} +9.17^\circ$ in H_2O ($p = 3.094$), $+14.32^\circ$ in EtOH ($p = 2.841$). The primary and sec. ions have $[\alpha]_D^{20} +6.73^\circ$ and -0.54° in H_2O respectively. *Me*₂ *d*- α -ethylglutarate, b.p. $111^\circ/16$ mm., $[\alpha]_D^{20} +14.63^\circ$. Partial racemisation occurs during the distillation of *d*-ethylglutaric anhydride, b.p. $147-148^\circ/12$ mm., $[\alpha]_D^{20} -23.16^\circ$. H. W.

Tartronic acid. B. BAK (Annalen, 1939, 537, 286-292).—Full directions are given for the conversion of *d*-tartaric acid into dinitrotartaric acid and thence by hot aq. EtOH into tartronic acid (I), m.p. $156-158^\circ$ when placed in a bath preheated to 130° and subsequently heated at a rate of 10° per min. Other methods of preparing (I) are reviewed.

H. W.

Optical activity and chemical structure in tartaric acid. Synthesis of cyclic derivatives of tartaric acid by condensing alkyl *d*-tartrates with aromatic aldehydes. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1939, 14, 35-40).—Interaction of *Et*₂ *d*-tartrate with the appropriate substituted PhCHO with P_2O_5 yields *Et*₂ *o*-nitro-, m.p. 60° , $[\alpha]_D^{20} +40.3^\circ$ in EtOH, $+116.3^\circ$ in C_6H_6 , $+6.9^\circ$ in cyclohexane (all $[\alpha]$ vals. below are in these solvents), *m*-nitro-, m.p. $43.5-44^\circ$, $[\alpha]_D^{20} -35.65^\circ$, -37.35° , -26.1° , *p*-nitro-, m.p. $59-59.5^\circ$, $[\alpha]_D^{20} -22.2^\circ$, -25.5° , -15.4° , *o*-hydroxy-, m.p. 59° , $[\alpha]_D^{20} -35.8^\circ$, -55.1° , -53.7° , *m*-hydroxy-, b.p. $207^\circ/0.5$ mm., m.p. $37-38.5^\circ$, $[\alpha]_D^{20} -32.5^\circ$, -26.1° , *p*-methoxy-, b.p. $183^\circ/0.3$ mm., $[\alpha]_D^{20} -27.86^\circ$, -26.87° , -18.3° , *o*-chloro-, m.p. $36-36.5^\circ$, $[\alpha]_D^{20} -15.9^\circ$, -28.6° , -22.1° , *m*-chloro-, b.p. $153^\circ/1$ mm., m.p. $29-30^\circ$, $[\alpha]_D^{20} -31.44^\circ$, -30.16° , -18.4° , *p*-chloro-, b.p. $180^\circ/0.5$ mm., $[\alpha]_D^{20} -28.1^\circ$, -26.8° , -14.7° , 3:4-methylenedioxy-, m.p. $40.5-41.5^\circ$, $[\alpha]_D^{20} -32.6^\circ$, -31.0° , -18.9° , benzylidene-*d*-dioxysuccinate. Similarly are formed *Et* cinnamylidene-, m.p. 54.4° , $[\alpha]_D^{20} -3.70^\circ$, -21.0° , 12.5° , *Pr*, b.p. $169^\circ/0.2$ mm., $[\alpha]_D^{20} -35.87^\circ$, *Bu*, b.p. $189-190^\circ/0.2$ mm., $[\alpha]_D^{20} -31.22^\circ$, and CH_2Ph benzylidene-*d*-dioxysuccinate, m.p. 86° , $[\alpha]_D^{20} -39.7^\circ$, -39.38° .

J. D. R.

Saccharolactone methyl ester. R. E. REEVES (J. Amer. Chem. Soc., 1939, 61, 664-665).—Pure saccharolactone and CH_2N_2 in cold MeOH- Et_2O give the lactone *Me* ester (I), m.p. $113-114^\circ$, $[\alpha] +29.0^\circ$ in H_2O (*CHPh* derivative, m.p. $237-238^\circ$, $[\alpha] +147^\circ$ in C_5H_5N), the structure of which is proved by cleavage by HIO_4 , followed by $Br-CaCO_3$, to $H_2C_2O_4$ and *d*-tartaric acid. With $N-KOH$ (I) gives *KH* saccharate (and the diamide) and with CH_2N_2 in Et_2O at 0° (1 week) yields the unsaturated lactone, m.p. $87-88^\circ$, $[\alpha]_D^{21} +79.5^\circ$ in MeOH, of Schmidt *et al.* (A., 1938, II, 42).

R. S. C.

Oxidation of gaseous formaldehyde.—See A., 1939, I, 268.

Photochemical oxidation of crotonaldehyde.—See A., 1939, I, 272.

Glyoxal tetramethyl acetal. D. H. GRANGAARD and C. B. PURVES (J. Amer. Chem. Soc., 1939, 61, 755).—A correction (cf. A., 1939, II, 140).

R. S. C.

Ether-like compounds. III. Cyclic ketals of acyclic ketones. E. J. SALMI and V. RANNIKKO (Ber., 1939, 72, [B], 600—604).—The following compounds are obtained by the method described previously (A., 1938, II, 427): *trimethylene*, $\text{CMe}_2\langle\begin{smallmatrix} \text{O}-\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{smallmatrix}\rangle\text{CH}_2$, b.p. 124—124.2°/758 mm., and *αγ-butylylene*, b.p. 130.0—131.2°, *ketals* of COMe_2 ; *ethylene*, b.p. 115.4—116.2°/763 mm., *αβ-propylylene*, b.p. 122.5—123.4°/759 mm., *trimethylene*, b.p. 146.2—147.0°/747 mm., and *αγ-butylylene*, b.p. 151.0—152.0°/766 mm., *ketals* of COMeEt ; *ethylene*, b.p. 88—89°/11 mm., *αβ-propylylene*, b.p. 84—86°/9 mm., *trimethylene*, b.p. 104—106°/10 mm., and *αγ-butylylene*, b.p. 81—82°/2 mm., *ketals* of *Me hexyl ketone*; *ethylene*, b.p. 147.0—147.5°/760 mm., *αβ-propylylene*, b.p. 55—56°/20 mm., *trimethylene*, b.p. 172.0—174.0°/737 mm., and *αγ-butylylene*, b.p. 57°/8 mm., *ketals* of *pinacolin*; *ethylene*, b.p. 155.0—156.0°/760 mm., and *αβ-propylylene*, b.p. 47.0—48.0°/9 mm., *ketals* of *mesityl oxide*. H. W.

Pinacolin change during the reduction of two molecules of mesityl oxide. Migration of methyl. Y. DEUX (Compt. rend., 1939, 208, 522—524; cf. A., 1938, II, 231; 1939, II, 46).— $\text{CMe}_2\text{CH}\cdot\text{COMe}$ with $\text{Mg}\cdot\text{Hg}$ at 100° affords a pinacol, transformed by loss of H_2O and migration of Me into *ε-keto-βδδγ-tetramethyl-Δ⁸-octadiene*, b.p. 105—107°/14 mm. (*semicarbazone*, m.p. 184°), which with $\text{EtOH}\cdot\text{KOH}$ at 110°/5 hr. affords *β-methylcrotonic acid*, m.p. 70° (*amide*, m.p. 108—109°; *anilide*, m.p. 128°), and *βδ-dimethyl-Δ⁸-pentene*, b.p. 81—83°/760 mm., converted by COCl_2 into a chlorohydrin which with KOH gives the *epoxide*, b.p. 130°/760 mm. The epoxide is isomerised at 500° into COPr^{β}_2 (*semicarbazone*, m.p. 145°). J. L. D.

Synthesis of aliphatic tert-butyl ketones. F. C. WHITMORE, C. I. NOLL, and V. C. MEUNIER (J. Amer. Chem. Soc., 1939, 61, 683—684).— $\text{Bu}^t\text{CO}\cdot\text{NH}_2$ and MgRX give good yields of Bu^t ketones if R is primary, but poor yields if R is *sec.*, and MgBu^tCl leads to 73% of Bu^tCN . Bu^t *ketozime*, m.p. 59.5—60.5°, Pr^t *Bu^t ketone* 2:4-dinitrophenylhydrazones, m.p. 116—116.5°, and Bu^t *n-amyl ketone* 2:4-dinitrophenylhydrazones, m.p. 99—100°, are incidentally described. R. S. C.

Synthesis of l-galactose. Structure of α- and β-diisopropylidenedulcitol. R. A. PIZZARELLO and W. FREUDENBERG (J. Amer. Chem. Soc., 1939, 61, 611—613).—l-Galactose (I) is prepared from citrus pectic acid by way of d-galacturonic acid etc. With 0.5% $\text{HCl}\cdot\text{COMe}_2$ dulcitol gives mainly β- (II), and with 0.5—1% acid mainly α-diisopropylidenedulcitol (III); with $\text{ZnCl}_2\cdot\text{H}_2\text{PO}_4\cdot\text{HPO}_3$ it gives 25% of (II) and 5.1% of (III). With $\text{Pb}(\text{OAc})_4$ (II) gives CH_2O and, with $\text{KMnO}_4\cdot\text{KOH}$, K diisopropylidene-l-galactonate, decomp. 195—200°, $[\alpha]^{25}_D + 51.2^\circ$ in H_2O , and thence (hot $\text{n-H}_2\text{SO}_4$; CdCO_3) Cd l-galactonate, decomp. 197—201°, the lactone, and (I). With $\text{Pb}(\text{OAc})_4$ (III) gives CH_2O and by KMnO_4 etc. K diisopropylidene-d-galactonate, m.p. 194—197°, $[\alpha]^{27}_D - 50.8^\circ$ in H_2O , Cd d-galactonate, and d-galactose. (II) is thus the 1:2:3:4- and (III) the 3:4:5:6-diisopropylidene derivative. R. S. C.

Derivatives of 3:4-monoacetone β-1:6-anhydrogalactose. D. MCCREATH and F. SMITH (J.C.S., 1939, 387—391).—The isolation of 3:4-isopropylidene-β-1:6-anhydrogalactose (I), m.p. 151—152°, $[\alpha]^{19}_D - 61.3^\circ$ in H_2O , -72.5° in CHCl_3 , $[\alpha]^{19}_D - 66.2^\circ$ in EtOH , as a by-product in the prep. of 1:2:3:4-diisopropylidenegalactose is described; it is identical with the isopropylideneanhydrogalactose of Micheel (A., 1929, 543). (I), Me_2SO_4 , and 30% NaOH give 2-methyl-3:4-isopropylidene-β-1:6-anhydrogalactose (II), a syrup, $[\alpha]^{17}_D - 84.5^\circ$ in EtOH , hydrolysed by $\text{EtOH}\cdot\text{H}_2\text{SO}_4$ to 2-methyl-β-1:6-anhydrogalactose, methylated to 2:3:4-trimethyl-β-1:6-anhydrogalactose (III), m.p. 61°, $[\alpha]^{19}_D - 69.2^\circ$ in EtOH . Hydrolysis of (III) (4% HCl) gives 2:3:4-trimethylgalactose, and of (II) (5% HCl) gives 2-methylgalactose (*anilide*, m.p. 165°).

[E. G. Cox and (Miss) A. I. WAGSTAFF]. X-Ray crystallographic data for β-1:6-anhydrogalactose and (I) are given. S. H. H.

aldehydo-d-Mannose penta-acetate ethyl hemiacetal. M. L. WOLFRAM, M. KONIGSBERG, and D. I. WEISBLAT (J. Amer. Chem. Soc., 1939, 61, 574—576).—An improved demercaptalation procedure leads to aldehydo-d-mannose hepta-acetate Et hemiacetal, m.p. 112—113°, $[\alpha]^{23}_D + 40.5^\circ \rightarrow +30^\circ$ in EtOH , $+34^\circ \rightarrow +20^\circ$ in CHCl_3 (no min.), which yields the known oxime and semicarbazone (m.p. 180°) of aldehydo-d-mannose penta-acetate. d-Mannonic acid penta-acetate, $+\text{H}_2\text{O}$, m.p. 68—70°, $[\alpha]^{21}_D + 23^\circ$ in CHCl_3 , and d-α-glucosheptonic acid hexa-acetate, $+\text{H}_2\text{O}$, m.p. 88—90°, $[\alpha]^{28}_D + 6^\circ$ in CHCl_3 , are obtained from the amides by NOCl in CHCl_3 . $[\alpha]^{23}_D$ of the anhyd. and hydrated forms of d-gluconic and d-galactonic acid penta-acetate [m.p. ($+\text{H}_2\text{O}$) 100—101°] are equal (cf. lit.), namely $+10$ — 11° and $+15$ — 16° , respectively; there is thus no evidence of ortho-acid forms. aldehydo-Maltose octa-acetate, m.p. 67—68°, $[\alpha]^{21}_D + 85^\circ$ in CHCl_3 , is reported. R. S. C.

Oxidations in the sugar group and their significance in sugar manufacture. O. SPENGLER, A. PFANNENSTIEL, and L. NORDSTRÖM (Z. Wirts. Zuckerind., 1939, 89, 171—205).—In presence of KOH , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, or $\text{Sr}(\text{OH})_2$ and catalysts such as Ag or Cu, sucrose (I) is rapidly and very extensively oxidised. In contrast to previous experiments in which more or less brown solutions result owing to caramelisation, the present solutions are colourless. An exception is met in solutions obtained from 1 mol. of (I) and 2 O, which are intensely yellow; the colour must be caused constitutionally since it disappears in the presence of more O. The change takes place rapidly at room temp. In hot, saturated aq. $\text{Sr}(\text{OH})_2$ the reaction can be so conducted that 18 O per mol. of (I) are absorbed in 4 hr. (75% of the amount required for the complete conversion of (I) into CO_2). Under these conditions 100 g. of (I) give 62 g. of $\text{H}_2\text{C}_2\text{O}_4$ and other products. Under mild conditions (I) is not hydrolysed in alkaline solution. Fission of the glucosidic linking is only possible therefore after oxidation of the intact mol. of (I). This fission necessitates the formation of oxidation products of the hexose components of (I). The isolation of K d-arabonate is recorded but high

yields are not to be expected since the salt rapidly undergoes further oxidation under the experimental conditions. In 2N-KOH at 50–60° (I) absorbs O₂ rapidly. At 70–80° the change is still faster; HCO₂H and CO₂ appear immediately but H₂C₂O₄ cannot be detected until 3–4 atoms of O per mol. of (I) have been absorbed. A mechanism of the reaction is proposed. The oxidation of glucose (II) and fructose (III) with mol. O₂ in aq. Ca(OH)₂ without catalyst proceeds differently from the change in aq. KOH under similar conditions whereby *d*-arabonic acid is obtained in 75% yield. In aq. Ca(OH)₂ (II) and (III) absorb respectively 3 O and 4 O whereas in 2N-KOH only 2.2 O are absorbed. Under like conditions (III) is much more rapidly and completely oxidised than is (II). The appearance of large amounts of H₂C₂O₄ in the evaporating plant of sugar refineries is explained by oxidative degradation of invert sugar or (I). H. W.

Pectic substances. II. Isolation of an araban from the carbohydrate constituents of pea-nut. III. Composition of apple pectin and molecular structure of the araban component. E. L. HIRST and J. K. N. JONES (J.C.S., 1939, 452–453, 454–460).—II. Separation of the two components of the pectic acid-araban complex present in the pea-nut (A., 1938, II, 221) is effected by extraction with 70% EtOH. Purification through the acetate, $[\alpha]_D^{20} -90^\circ$ in COMe₂, gives the *araban* (I), $[\alpha]_D^{20} -160^\circ$ in H₂O. Hydrolysis gives *l*-arabinose (96% yield), the rate indicating that the arabinose residues are exclusively furanose in type.

III. The pectin from apple pomace is a mixture of Me pectate (II) (49.2%), araban (III) (20%), and galactan (IV) (~30%). Hydrolysis (0.05N-H₂SO₄) gives a (II)–(IV) complex; the pectic acid, $[\alpha]_D^{20} +276^\circ$ in NaOH, separated through the Na salt is composed (96.7%) of anhydrogalacturonic acid residues. By preferential methylation *methylaraban*, $[\alpha]_D^{20} -86^\circ$ in MeOH, is obtained, which on hydrolysis gives equimol. proportions of 2:3:5-trimethyl-, 2:3-dimethyl-, and 3-methyl-*l*-arabinose. These sugars are joined in the furanose form in (III). The constitution of (III) is discussed, the main features of its structure being identical with those of (I). S. H. H.

Constitution and crystalline structure of cellulose. K. H. MEYER (Österr. Chem.-Ztg., 1939, 42, 7–10).—An account is given of the differences between celluloses in terms of the average length and distribution of lengths of the mol. chains, the presence of units of xylan or glycuronic acid, the size and orientation of the micelles, and the compactness of the lattice. W. A. R.

Formation of quaternary ammonium salts from dihalogeno-paraffins etc. in aqueous acetone solution. W. C. DAVIES, (Miss) E. B. EVANS, and F. L. HULBERT (J.C.S., 1939, 412–418).—The reaction between NMe₃ and CH₂Br₂, (CH₂Br)₂, and Br-[CH₂]₃-Br in aq. COMe₂ is bimol. and leads to the monoquaternary NH₄ salt. When the base is in excess, a consecutive reaction giving the diquaternary NH₄ salt takes place. The formation of the latter is investigated separately. The reactiv-

ities of halides towards NMe₃ (the reaction of only one of the halogen atoms * being considered) are: EtCl > Cl-CH₂Cl > Cl-[CH₂]₂Cl. MeBr > Br-CH₂Br ~ Br-[CH₂]₂-Br. Br-[CH₂]₃-Br > Br-[CH₂]₂-Br > Br-NMe₃[CH₂]₂-Br. Br-NMe₃[CH₂]₃-Br > Br-NMe₃[CH₂]₂-Br. Br-[CH₂]₃-Br =

Br-NMe[CH₂]₃-Br. These relative reactivities are discussed with reference to the reactivities of other halides with NMe₃ and to the mechanism of NH₄ salt formation. S. H. H.

Dimethylaminoisoprene. C. MANNICH and O. SALZMANN (Ber., 1939, 72, [B], 506–510).—NHMe₂, CH₂O, and COMe₂ give dimethylaminobutanone and, mainly, α -dimethylamino- β -dimethylaminomethylbutan- γ -one, b.p. 91°/14 mm. (dihydrobromide, m.p. 150–250° according to rate of heating), reduced by Na-Hg in acid solution to α -dimethylamino- β -dimethylaminomethylbutan- γ -ol (I), b.p. 98°/15 mm. [dihydrobromide, m.p. 248–249°; perchlorate, m.p. 195°; feebly anaesthetising benzoate hydrochloride, m.p. 250° (decomp.)]. Hofmann degradation of the dimethiodide, m.p. 251°, leads to trimethyl- γ -hydroxy- β -methylene-*n*-butylammonium hydroxide, isolated as the perchlorate, m.p. 102–103°. Red P and HI (*d* 1.7) at 200° transform (I) into α -dimethylamino- β -dimethylaminomethyl-*n*-butane, b.p. 184°/atm. pressure, 70°/12 mm. [dihydriodide, m.p. 224° (decomp.)]; hydrobromide, m.p. 243°. α -Dimethylamino- β -dimethylaminomethylbutan- γ -ol hydrochloride is transformed by boiling SOCl₂ into γ -chloro- α -dimethylamino- β -dimethylaminomethylbutane, b.p. 82°/12 mm. [dihydrochloride, m.p. ~200° (decomp.)]. This is converted by 30% NHMe₂ and Cu-bronze at 160° into $\alpha\gamma$ -tetramethyldiamino- β -dimethylaminomethylbutane, b.p. 100°/20 mm. [dihydriodide; trinitrate, m.p. ~135° (much decomp.)]. The triamine and MeI in MeOH at 100° afford the hydriodide dimethiodide, NMe₃I-CHMe-CH(CH₂-NMe₃)₂-CH₂-NMe₃I, m.p. 211°, which is degraded to trimethyl- β -dimethylaminomethyl- Δ^2 -butenylammonium hydroxide, isolated as the aurichloride, m.p. 212°, and platinichloride, m.p. 220°, a small amount of dimethylaminoisoprene, b.p. ~101°/760 mm. (hydrobromide, m.p. 231°), which appears to form an NH₂-acid by diene synthesis from maleic anhydride, and dimeric dimethylaminoisoprene, b.p. 130°/11 mm. (dimethiodide, m.p. 245°); the hydrochloride is hydrogenated to the base, C₁₄H₃₂N₂ best isolated as the diaurichloride, m.p. 191°.

H. W.

Dimethylaminodihydroxypentane and dimethylaminotrihydroxyhexane. C. MANNICH and O. SALZMANN (Ber., 1939, 72, [B], 499–505).—Attempts to extend the Tollens reaction to β -NH₂-ketones are described. CH₂Ac-CH₂-NMe₂ and CH₂O [the alkalinity of the base renders addition of Ca(OH)₂ superfluous] give unchanged base, CHAc(CH₂-NMe₂)₂, and basic components which are too unstable to be identified. The crude product is therefore reduced by Na-Hg, thus giving unaltered material, α -dimethylamino- β -dimethylaminomethylbutan- γ -ol, dihydroxy-(I) and trihydroxy-(II) -bases. (I) is benzoylated and then converted into the hydrobromide, which

affords the α -form of α -dimethylamino- γ -benzoyloxy- β -benzoyloxymethylbutane hydrobromide (III), m.p. 224°, when cryst. successively from COMe₂ and MeOH. (III) is hydrolysed to the α -variety of α -dimethylamino- β -hydroxymethylbutan- γ -ol (IV), b.p. 133—135°/12 mm. (hydrobromide, m.p. 113°; methiodide, m.p. 115°), which could not be converted by HI into an O-free amine. SOCl₂ and (IV) in CHCl₃ give the α -form of γ -chloro- α -dimethylamino- β -chloromethylbutane, b.p. 80°/12 mm. (hydrobromide, m.p. 164°); the corresponding hydrochloride, m.p. 165°, is quantitatively converted by 30% NHMe₃ and Cu-bronze at 160° into α - γ -didimethylamino- β -dimethylaminomethylbutane, b.p. 91°/12 mm., characterised further as the dihydriodide and trinitrate. The mother-liquors from (III) give a mixture of bases (V) so far enriched in the β -form that it is possible to isolate the methiodide, m.p. 140°, of the β -variety of α -dimethylamino- β -hydroxymethylbutan- γ -ol. SOCl₂ in CHCl₃ transforms (V) into a mixture of Cl-bases from which the β -form of γ -chloro- γ -dimethylamino- β -chloromethylbutane, b.p. 78°/11 mm. (hydrochloride, m.p. 129—131°; hydrobromide, m.p. 148—149°), is separated. Either Cl₂-base is converted by NaI in COMe₂ followed by AgCl into dimethyl- β -chloroethyltrimethylenammonium chloride (VI), CHMeCl-CH< $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ >NMe₂Cl (isolated as the aurichloride, m.p. 133°), reconverted by distillation under diminished pressure into the mixture of Cl₂-bases. Treatment of (VI) with Ag₂O followed by distillation in vac. affords γ -chloro- α -dimethylamino- β -methylenebutane, b.p. 86°/46 mm. (hydrochloride, m.p. 179°). MeI slowly transforms (II) into trimethyl- γ - ϵ -dihydroxy- β -hydroxymethylamylammonium iodide, m.p. 114°, converted by P and conc. HI at 280° into NMe₃ and an oil with an odour of petroleum. Boiling Ac₂O containing NaOAc transforms (II) into the Ac₃ derivative, b.p. ~185°/15 mm. (methiodide, m.p. 173—174°). H. W.

Preparation and properties of uncharged glycine. S. J. VON PRZYLECKI, M. KOŁACZKOWSKA, and W. GIEDROYĆ (Biochem. Z., 1939, 300, 128—135; cf. A., 1937, II, 8; Edsall and Blanchard, A., 1933, 781).—Powdered anhyd. glycine dissolved in AcOH and pptd. with abs. Et₂O is converted into the uncharged mol., ρ 1.501—1.544, which gives an X-ray picture different from that of the zwitterion, some of which contaminates the uncharged mol. The change from uncharged mol. to zwitterion is completely reversible. W. McC.

Monohydrochloride, + H₂O, m.p. 136°, anhyd., m.p. 232—233° (decomp.), of α -N-dimethyllysine.—See A., 1939, III, 397.

Hydrolytic fission of the disulphide linking in cystine derivatives, glutathione, and insulin. A. SCHÖBERL and P. RAMBACHER (Annalen, 1939, 538, 84—98).—All cystine (I) derivatives are decomposed by alkali essentially into thiol and sulphenic acid. According to the temp. and concn. of alkali secondary reactions occur whereby the labile SH compounds yield H₂S, possibly according to CHRR'·CH₂·SH \rightarrow CRR'·CH₂ + H₂S. Elementary S is probably derived from sulphenic acids, CHRR'·CH₂·S·OH \rightarrow S + CHRR'·CH₂·OH. All

sulphenic acids appear capable of stabilisation with elimination of H₂S or S. At 60°, (I) does not give H₂S but, after long periods, cysteine is found in considerable amount. Dialanylecystine gives 4.1% of H₂S at 80° and 23.6% at the b.p. of the mixture. Dicarbobenzoyloxycystinylglycine is completely decomposed by N-alkali in 15 min. at 40° giving 14.4% of H₂S and 25.2% of SH compound. Equimol. quantities of H₂S and thiol are thus not obtained. Cystinehydantoin is completely decomposed by N-alkali within 120 min. at 40° without formation of the SH compound. With 0.1N-alkali at 40° in 15 min. 4.4% of H₂S and 46.4% of SH compound are produced. Rise of temp. to 60° causes an increase of H₂S to 11.3% and diminution of the SH val. to 26.0%. Dialanylecystine dianhydride at low temp. with 0.1N- or N-alkali gives the corresponding SH compound in good yield whilst rise of temp. causes an increase in the yield of H₂S and diminution in that of SH. Fission of SS-glutathione by N-alkali occurs quantitatively at 30° with formation of about 50% of SH-glutathione, whereas at the b.p. H₂S is produced exclusively. Between these limits with rise in temp. there is a continuous diminution of the SH val. paralleled by a continuous increase in the H₂S yield. H. W.

dl-Methionine sulfoxide. F. MICHEEL and H. SCHMITZ (Ber., 1939, 72, [B], 518).—dl-Methionine is converted by AcO₂H containing a little H₂SO₄ at 0° and then at room temp. into dl-methionine sulfoxide, m.p. 241—242° (decomp.). H. W.

Synthesis of alkyl-substituted carbamides. F. A. GRINBERG (Prom. Org. Chim., 1939, 6, 31—33).—NH₂·CO·NH·NO₂ and NH₂Me give NH₂·CO·NHMe in 50% yield. Known methods for prep. of CO(NHMe)₂ are described. R. T.

Attempted preparation of sulphoacetic ureides. K. BODENDORF and N. SENGEL (Ber., 1939, 72, [B], 571—576).—Addition of SO₃Et·CH₂·CO₂Et (I) and CO(NH₂)₂ to NaOEt·EtOH gives Na ureidosulphoacetate, which is mainly unchanged when heated with PCl₅ or POCl₃. Definite products are not obtained when (I) is heated with CO(NH₂)₂ at 100—105°. SO₃H·CH₂·CO₂H is transformed by an excess of hot SOCl₂ into sulphoacetyl dichloride (I), SO₂Cl·CH₂·COCl, b.p. 86—87°/1 mm., in 36% yield; better yields are obtained by use of PCl₅ but the product is freed with difficulty from P compounds. With NH₂Ph in C₆H₆ it affords the dianilide (II), m.p. 151°. When triturated with CO(NH₂)₂ (I) gives the semi-solid product, NH₂·CO·NH·CO·CH₂·SO₂Cl, transformed by EtOH into Et ureidosulphoacetate, m.p. 168°, and by excess of NH₂Ph into ureidosulphoacetanilide, m.p. 204—205°, which is converted into (II) by NH₂Ph at 200°. Aspiration of moist air through a solution of (I) in C₆H₆ leads to sulphoacetyl chloride, m.p. 76—78°, transformed by CO(NH₂)₂ into the carbamide salt of ureidosulphoacetic acid and by NH₂Ph into anilinium anilidosulphoacetate, m.p. 234°. H. W.

Preparation and properties of high-mol. wt. aliphatic thioamides. A. W. RALSTON, R. J. VAN DER WAL and M. R. MCCORKLE (J. Org. Chem.,

1939, 4, 68—70).—EtOH saturated with H_2S and NH_3 at 0° is added to stearonitrile (I) in a steel bomb and the mixture is heated at 160° , giving *thiostearamide* (II), m.p. $96-97^\circ$. *Thiolauramide*, m.p. $82-83^\circ$, *thiomyristamide*, m.p. $87-88^\circ$, and *thiopalmamide*, m.p. $93-94^\circ$, are obtained similarly. Na and Bu^iOH reduce (I) to octadecylamine. $KOH-EtOH$ or boiling 80% H_2SO_4 hydrolyses (I) to stearic acid. At $175-200^\circ$ (II) passes into (I) and H_2S . H. W.

Constitution of the tetrapolymeride of hydrogen cyanide. L. E. HINKEL (J.C.S., 1939, 492—493).—A reply to Gryszkiewicz-Trochimowski (A., 1938, II, 434). F. R. S.

α -Hydroxylaminoisobutyronitrile, an intermediate in the synthesis of porphyraxide and porphyrindine. C. C. PORTER and L. HELLERMAN (J. Amer. Chem. Soc., 1939, 61, 754).— $OH-NH-CMe_2-CN$ (25 g.) is conveniently prepared by adding an excess of aq. NaCN to CMe_2N-OH (94.9 g.) in H_2O buffered by KH_2PO_4 . R. S. C.

Boron hydrides. XI. Reaction of diborane with organic compounds containing a carbonyl group. H. C. BROWN, H. I. SCHLESINGER, and A. B. BURG (J. Amer. Chem. Soc., 1939, 61, 673—680).— B_2H_6 reacts rapidly with simple aldehydes and ketones and slowly with esters such as HCO_2Me and $EtOAc$ to form dialkoxyboranes by addition. No reaction occurs between B_2H_6 and acid chlorides or chloral (I). BF_3 forms complex compounds with $COMe_3$, $MeCHO$, Bu^iCHO , (I), and $AcCl$ by addition to CO . The relative stabilities of these compounds are a measure of the electron donor properties of CO . A correlation exists between the ability of CO to react with B_2H_6 or to add BF_3 , which is explained by a proposed mechanism of addition. The prep. of *diethoxyborane*, *diisopropoxyborane*, *dineopentoxyborane*, and the *additive compounds* (1:1) of BF_3 with (I), $MeCHO$, and Bu^iCHO is described. The decomp. pressures of additive compounds of BF_3 with $AcCl$ and (I) have been determined at -83.8° to -60.2° and -78.2° to -53.7° respectively. E. S. H.

Production of cyclopropane.—See B., 1939, 355.

Hydr[ogen]ation of aromatic hydrocarbons by Skita's method.—See A., 1939, I, 271.

Mechanism of catalytic hydrogenation of phenol under high pressure. V. Effect of reaction temperature and pressure on the composition of hydrocarbons formed. S. ANDO (J. Soc. Chem. Ind. Japan, 1938, 41, 413—414B; cf. A., 1939, II, 146).—As observed previously, PhOH was completely converted into neutral oil, of which 82—93% was composed of C_6H_8 , cyclohexane, and methylcyclopentane (I). The C_6H_8 content of this main fraction varied but little with temp. but decreased with pressure. The higher was the reaction temp., the larger was the % of (I) in the saturated hydrocarbon fraction. Although the % of saturated hydrocarbons in the main fraction increased with pressure, the composition of the saturated hydrocarbon fraction remained substantially the same. H. C. M.

Reaction of paraffins with hexahydroaromatic hydrocarbons in presence of aluminium halides. H. PINES, A. V. GROSSE, and V. N. IPATIEV (J. Amer. Chem. Soc., 1939, 61, 640—643).— $CHMeEtBu^i$, $CH_2Pr^iBu^i$, or $(CHMeEt)_2$, but not $n-C_8H_{16}$ or $CHMe_2Bu^i$, reacts with cyclohexane (I) or methylcyclohexane and $AlCl_3$ or $AlBr_3$ at 65° to give isobutane, polymethyl- and methylethyl-cyclohexanes, but side-reactions also occur, e.g., $CHMeEtBu^i \rightarrow CHMe_3 + CHEtCH_2$; $CHEtCH_2 + 2(I) \rightarrow (C_6H_{11})_2 + n-C_4H_{10}$; $n- \rightarrow iso-C_4H_{10}$. R. S. C.

Catalytic oxidations. II. Oxidations in the cycloparaffin series. N. A. MILAS and W. L. WALSH (J. Amer. Chem. Soc., 1939, 61, 633—635; cf. A., 1935, 1246).—Catalytic oxidation of cyclohexene, -hexane, -hexanone, -hexanol, -pentane, or -pentadiene, or adipic acid by air gives only maleic acid. Optimum conditions (temp. varying between 328° and 410°) and max. yields (14.8—32.4%) using V_2O_5 -pumice are detailed, and possible reaction mechanisms are discussed. R. S. C.

Dehydrogenative, hydrogenative, and irreversible catalysis of the dimeride of butadiene (1-vinyl- Δ^3 -cyclohexene). S. R. SERGIENKO (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 753—759).—With Pt- or Pd-asbestos, Pd-C, or Ni- Al_2O_3 at $135-150^\circ$, the dimeride of butadiene reacts irreversibly as follows: $3C_8H_{12} \rightarrow 2PhEt + C_6H_{11}Et$. Above 160° the dehydrogenation begins to predominate, and at $300-310^\circ$ PhEt is obtained in 95% yield (using Pd-C or Ni- Al_2O_3). A. LI.

Condensation of propene and isobutene with benzene in presence of anhydrous ferric chloride. W. M. PORTS and L. L. CARPENTER (J. Amer. Chem. Soc., 1939, 61, 663—664).—At room temp. (not at 80°) in presence of anhyd. $FeCl_3$ (0.3 mol.), CMe_3CH_2 (1 mol.) and C_6H_6 give 89% of $PhBu^i$; 2 mols. of CMe_3CH_2 give 65% of $p-C_6H_4Bu^i_2$. C_3H_8 , an excess of C_6H_6 , and $FeCl_3$ (0.3 mol.) give 91% of $PhPr^i$. Less polymerisation occurs than when $AlCl_3$ is used. R. S. C.

Mechanism of high-temperature hydrogenation of aromatic hydrocarbons. VI. Isomerisation of anthracene and phenanthrene perhydrides under conditions of high-temperature hydrogenation, and in presence of anhydrous aluminium chloride. E. I. PROKOPETZ. VII. Product of high-temperature hydrogenation of benzene. E. I. PROKOPETZ, A. N. FILARETOV, and S. M. BOGUSLAVSKAJA (J. Appl. Chem. Russ., 1938, 11, 1471—1474, 1475—1480).—VI. Liquid perhydro-anthracene and -phenanthrene are converted into solid perhydroanthracene, m.p. $90-90.5^\circ$, by hydrogenation at $380^\circ/100$ atm. (MoS_2 catalyst), or by heating with $AlCl_3$; the processes are reversible.

VII. Hydrogenation of C_6H_6 at $450^\circ/200$ atm. (1:1 MoS_2 -kaolin catalyst) gives cyclohexane and -pentane, methylcyclopentane, iso-pentane and -hexane. R. T.

Optical isomerism due to symmetrically placed hydrogen and deuterium atoms. II. G. R. CLEMO, R. RAPER, and A. C. ROBSON (J.C.S.,

1939, 431—435; cf. A., 1936, 977).—Allenes depending for possible asymmetry on the difference of Ph from C_6D_5 were obtained only in inactive forms by dehydrating allyl alcohols by optically active acids. Addition of $COPh \cdot CH \cdot CPh \cdot C_{10}H_7 \cdot \alpha$ (I) in C_6H_6 to $MgPhBr \cdot Et_2O$ gives $\alpha\gamma$ -triphenyl- γ -1-naphthylallyl alcohol, m.p. 150°, converted by a little *d*-camphor-sulphonic acid (II) in hot C_6H_6 or more slowly by *d*-tartaric or *l*-mandelic acid (III) in hot EtOH into $\alpha\gamma$ -triphenyl- γ -1-naphthylallene, dimorphous, m.p. 100—102° and 142°, but by *p*- $C_6H_4Me \cdot SO_3H$ (IV) into 1:1:3-triphenyl-4:5-benzindene, m.p. 234°. $C_6D_5 \cdot MgBr$ and (I) give similarly $\alpha\gamma$ -diphenyl- α -pentadeuterophenyl- γ -1-naphthylallyl alcohol, m.p. 149—150°, and thence by (II) $\alpha\gamma$ -diphenyl- α -pentadeuterophenyl- γ -1-naphthylallene (V), dimorphous, m.p. 100—101° and 142°, α . CH_2Bz_2 and $MgPhBr$ give β -hydroxy- $\beta\beta$ -diphenylpropionophenone, m.p. 116—118°, converted by hot HCl or, more rapidly, hot HCO_2H (*d* 1.2) into *Ph* $\beta\beta$ -diphenylvinyl ketone, m.p. 88°. This with 1- $C_{10}H_7 \cdot MgBr$ yields $\alpha\gamma$ -triphenyl- α -1-naphthylallyl alcohol, m.p. 124—126°. CH_2Bz_2 and $C_6D_5 \cdot MgBr$ give similarly β -hydroxy- β -phenyl- β -pentadeuterophenylpropionophenone, m.p. 115°, and thence by HCO_2H *Ph* β -phenyl- β -pentadeuterophenylvinyl ketone, m.p. 85—86°; 1- $C_{10}H_7 \cdot MgBr$ then yields $\alpha\gamma$ -diphenyl- γ -pentadeuterophenyl- α -1-naphthylallyl alcohol, m.p. 117—119°, which with (II) yields (V). *p*- $C_6H_4Me \cdot MgBr$ and (I) give $\alpha\gamma$ -diphenyl- α -*p*-tolyl- γ -1-naphthylallyl alcohol, m.p. 131—133°; (II) then gives $\alpha\gamma$ -diphenyl- γ -*p*-tolyl- α -1-naphthylallene (VI), m.p. 119—122°, and 1:3-diphenyl-1-*p*-tolyl-4:5-benzindene (VII), m.p. 172—175°; (III) affords (VI), but (IV) gives (VII). (VI) is converted into (VII) by HCl-AcOH. CH_2Bz_2 and *p*- $C_6H_4Me \cdot MgBr$ give β -hydroxy- β -phenyl- β -*p*-tolylpropionophenone, m.p. 109—111°, and thence by aq. HCl *Ph* β -phenyl- β -*p*-tolylvinyl ketone, forms, m.p. 108—109° (*cis* with respect to H and *p*-tolyl; μ 1.00) and 85° (*trans*; μ 0.88). 1- $C_{10}H_7 \cdot MgBr$ then gives $\alpha\gamma$ -diphenyl- γ -*p*-tolyl- α -1-naphthylallyl alcohol, m.p. 150—152°, converted by (III) or (II) into (VI), and by (IV) into (VII). $\alpha\gamma$ -Diphenyl- $\alpha\gamma$ -di-1-naphthylallyl alcohol in hot C_6H_6 is slowly asymmetrically dehydrated by *d*- or *l*-(III) or by *d*-tartaric acid, giving optically active solutions (cf. Maitland *et al.*, A., 1936, 1100). R. S. C.

Leprotene, a carotenoid of the formula $C_{40}H_{54}$. Y. TAKEDA and T. OHTA (Z. physiol. Chem., 1939, 258, 6—8; cf. A., 1937, III, 100).—Crude leprotene (I) (yield 10 mg.) is obtained from 800 g. of the dried bacteria by a process including extracting with $COMe_2$, hydrolysis, pptn. from light petroleum with EtOH, and crystallising from C_6H_6 -MeOH. Crude (I) in light petroleum is purified by adsorption on Al_2O_3 and elution with C_6H_6 -light petroleum, impurities being removed by adsorption on $CaCO_3$. (I), $C_{40}H_{54}$, absorbs 12 H_2 on hydrogenation, is a provitamin-A, and is probably a dehydro- β -carotene. W. McC.

Diphenylnaphthalenes. (Miss) H. M. CRAWFORD (J. Amer. Chem. Soc., 1939, 61, 608—610).—1:2- (I), 1:3- (II), and 2:3-Diphenylnaphthalene (III) are synthesised. $CH_2Bz \cdot CHPh \cdot CO_2H$ (prep. from $CHPh \cdot CH \cdot CPh$ by way of $CH_2Bz \cdot CHPh \cdot CN$) with Zn-Hg-HCl gives 75% of

$CH_2Ph \cdot CH_2 \cdot CHPh \cdot CO_2H$, m.p. 75° (cf. lit.), which with H_2SO_4 -AcOH at 100° gives 57% of 1-keto-2-phenyl-1:2:3:4-tetrahydronaphthalene, m.p. 79—80° (Newman, A., 1939, II, 55, m.p. 76.2—77°). With $MgPhBr$ in Et_2O this yields 53% of 1-hydroxy-1:2-diphenyl-1:2:3:4-tetrahydronaphthalene, m.p. 98—99°, which with HCl-EtOH gives 1:2-diphenyl-3:4-dihydronaphthalene, m.p. 76.5—77°, dehydrogenated by Se at 260—280° to (I), m.p. 109.5—110°. 1-Keto-3-phenyl-1:2:3:4-tetrahydronaphthalene (prep. in 40% yield from $CH_2Ph \cdot CHPh \cdot CH_2 \cdot CO_2H$ by H_2SO_4 -AcOH), m.p. 65°, with $MgPhBr$, followed by HCl-EtOH, gives 1:3-diphenyl-3:4-dihydronaphthalene (81% yield), m.p. 136°, and thence (Se at 260°) 60% of (II), m.p. 70—71°. $CH_2Ph \cdot [CHPh]_2 \cdot CO_2H$, m.p. 153—154°, obtained in 30% yield from $CHBzPh \cdot CHPh \cdot CO_2H$ by Zn-Hg-HCl, is cyclised by H_2SO_4 -AcOH (25%), or $SOCl_2$ followed by $AlCl_3$ in CS_2 (58%), to 1-keto-2:3-diphenyl-1:2:3:4-tetrahydronaphthalene, m.p. 146—147°. Clemmensen reduction then yields 2:3-diphenyl-1:2:3:4-tetrahydronaphthalene (50%), m.p. 129—129.5°, and thence by Se at 310—325° (not 260—280°) (III), m.p. 86—87°. R. S. C.

Synthesis of 12-methylperhydropretene (abietane) and its non-identity with fichtelite. E. C. STERLING and M. T. BOGERT (J. Org. Chem., 1939, 4, 20—28).—12-Methylperhydropretene (I) [1:12-dimethyl-7-isopropyltetradecahydrophenanthrene] has been synthesised as a colourless, viscous liquid which is therefore not identical with the fossil resin, fichtelite (cf. Ruzicka *et al.*, A., 1935, 741). It appears identical with a perhydroabietene (abietane) obtained by catalytic hydrogenation of abietene at high temp. and high pressure. Gradual addition of HNO_3 (*d* 1.42) and H_2SO_4 (*d* 1.84) to cumene at 10—20° gives *o*- (19%) and *p*- (73%) -nitrocumene and 8% of 2:4-dinitrocumene, b.p. 136°/2 mm., m.p. 18.5° (all m.p. are corr.). *p*-Cumidine, b.p. 222.5°, and Ac_2O in dil. AcOH give the Ac derivative, m.p. 102.5°, brominated in glacial AcOH at 45° to 3-bromo-4-acetamidocumene, m.p. 129°. 3-Bromo-4-aminocumene, b.p. 141—143°/16 mm. [hydrochloride, m.p. 190—195° (decomp.)], is deaminated to *m*-bromocumene, b.p. 208—210°. *m*- $C_6H_4Pr^s \cdot MgBr$ and $(CH_2)_2O$ afford β -*m*-cumylethanol, b.p. 124°/10 mm. (3:5-dinitrobenzoate, m.p. 82°), and this with PBr_3 gives β -*m*-cumylethyl bromide, b.p. 120°/10 mm., which is condensed (Grignard) with 2:6-dimethylcyclohexanone to 1- β -*m*-cumylethyl-2:6-dimethylcyclohexanol, b.p. 144—146°/2 mm., which could not be caused to give a phenylurethane or a 3:5-dinitrobenzoate. It is cyclised by 85% H_2SO_4 to 12-methyl-1:2:3:4:9:10:11:12-octahydroretene, b.p. 180°/12 mm. (dehydrogenated by Se at 300° to retene), which is hydrogenated (Raney Ni in methylcyclohexane at 225°/150 atm.) to (I), b.p. 179—180°/12 mm. H. W.

1:4:9:10-Tetraphenylnanthracene. C. WEIZMANN and E. BERGMANN (J.C.S., 1939, 494—495).—9:10-Dihydroxy-1:4:9:10-tetraphenyl-9:10-dihydroanthracene and H_2SO_4 -MeOH (probably in hot MeOH alone) give the *Me_2* ether, m.p. 309°, which with Na in Et_2O gives the 9:10- Na_2 derivative of 1:4:9:10-tetraphenyl-9:10-dihydroanthracene (I),

converted by Hg in N₂ into 1 : 4 : 9 : 10-tetraphenyl-anthracene or by EtOH-Et₂O into (I), *cis*- and *trans*-forms, m.p. 217° and 205°.

R. S. C.

Characterisation of simple and carcinogenic aromatic hydrocarbons through the density distribution of certain valency electrons (*B* electrons). II.—See A., 1939, I, 183.

Labile union of oxygen with carbon. C. DUFRAISSE (Bull. Soc. chim., 1939, [v], 6, 422—456).—A lecture.

9-Phenyl-1 : 2 : 3 : 4-dibenzanthracene. E. BERGMANN and T. BERLIN (J.C.S., 1939, 493—494).—*o*-9-Phenanthrylbenzoic acid and Hg-Zn wool in HCl give *ω*-9-phenanthryl-*o*-toluic acid, m.p. 197°, converted by SOCl₂, followed by AlCl₃ in CS₂ at 0°, into 1 : 2 : 3 : 4-dibenz-9-anthrone, m.p. 286°. LiPh in Et₂O-N₂ at room temp. then gives 9-hydroxy-9-phenyl-9 : 10-dihydro-1 : 2 : 3 : 4-dibenzanthracene, m.p. 250° (decomp.), dehydrated by hot BuOH-conc. HCl to 9-phenyl-1 : 2 : 3 : 4-dibenzanthracene.

R. S. C.

Perylene trihalides. K. BRASS and E. CLAR (Ber., 1939, 72, [B], 604—607).—In reply to Zinke *et al.* (A., 1937, II, 142) it is shown that the primary product of the action of Br on perylene (I) in C₆H₆ is not a normal tetrabromide but an abnormal tribromide. The compound obtained by Zinke by the action of Br vapour on (I) is regarded as an additive compound of bromoperylene and Br. The composition of perylene tri-iodide is established exactly by analysis.

H. W.

Unsaturated steroids. VI. Structure of 3-chloro- and 3-phenyl-cholestadiene. W. BERGMANN and F. HIRSCHMANN (J. Org. Chem., 1939, 4, 40—47).—Study of the properties of ergosterol, Δ^{2:4} and Δ^{2:5}-cholestadiene suggests the following rules as guides in determining whether a diene has a system of conjugation restricted to one ring or extending over two rings (*A* and *B* respectively). *A* show selective absorption of ultra-violet light with max. in the region of 265—280 mμ. whereas *B* show max. absorption in the region 230—245 mμ. *A* give normal additive products with maleic anhydride whereas *B* may react but only in such a manner as to give complex products of high mol. wt. *A* add 1 mol. of H₂ when treated with Na in EtOH whereas *B* are not reduced under these conditions. *A* are unstable towards dil. acid, in which they rearrange to stable compounds, preferably dienes *B*. *A* add O₂ in presence of light and a sensitiser such as eosin to give transannular peroxides; *B* do not react thus. Steroids containing a Δ⁴-double linking always have positive rotations whereas their Δ⁵-isomerides have negative rotations. Application of these rules shows that the product obtained by Urushibara *et al.* (A., 1937, II, 416) from cholestenone (I) and MgPhBr is 3-phenyl-Δ^{3:5}-cholestadiene (II). Decomp. of the product from (I) and MgPhBr with NH₄Cl leads to 3-hydroxy-3-phenyl-Δ⁴-cholestene, m.p. 103—105.5°, [α]_D²⁵ +75.5° in Et₂O, which could not be dehydrated under neutral or slightly alkaline conditions to the Δ^{2:4}-compound; in all circumstances (II) is obtained. The product, m.p. 62—63°, [α]_D²⁵ -117.5°

M** (A., II.)

in CHCl₃, of the interaction of (I) and BzCl at 100° is 3-chloro-Δ^{3:5}-cholestadiene (cf. Ruzicka *et al.*, A., 1936, 991). All m.p. are corr.

H. W.

Acid catalysis in amines. I. Catalytic effect of cyclohexylammonium salts on the reaction between cyclohexylamine and esters. P. K. GLASOE and L. F. AUDRIETH (J. Org. Chem., 1939, 4, 54—59).—An excess of cyclohexylamine (I) reacts with an NH₄ salt at 100° with evolution of NH₃, which occurs with decreasing readiness in the sequence, NH₄NO₃ > NH₄I > NH₄Br > NH₄Cl. cyclohexylammonium bromide, m.p. 196—197°, and nitrate, m.p. 156°, are thus obtained. NH₄I gives the salt, (C₆H₁₁·NH₂)₂·HI, m.p. 185—187°, which passes when cryst. from EtOH into cyclohexylammonium iodide (II), m.p. 193—194°. The rate of reaction of (I) on esters is measured by treating samples of the reaction mixture after definite times with an excess of standard HCl and back-titrating with alkali. In the cases studied the rate increases in the sequence, EtOAc, CH₃Ph·CO₂Et, OH·CHMe·CO₂Et, and CH₃(CO₂Et)₂; in all cases the change is greatly accelerated by (II). Malondi, m.p. 175°, phenylacet., m.p. 134°, and lact., m.p. 59°, -cyclohexylamide are described.

H. W.

Variation of the colour of *p*-nitroacetanilide on diluting its solution in sulphuric and nitric acids. J. F. SALELLAS (Rev. Fac. Cienc. Quim. La Plata, 1937, 12, 79—81).—Pure *p*-NHAc·C₆H₄·NO₂ (I) is colourless. Yellow samples are presumed to contain *p*-NH₂·C₆H₄·NO₂ formed by hydrolysis. The existence of a compound of (I) and H₂SO₄ (cf. Nörling and Collin, A., 1884, 1011) could not be confirmed.

F. R. G.

Diazotisation and nitrosation of amines. II. Changes in hydrogen-ion concentration during the reaction. J. C. EARL and C. S. RALPH. III. Aromatic amine nitrites and their decomposition. J. C. EARL and C. H. LAURENCE (J.C.S., 1939, 401—403, 419—420; cf. A., 1939, I, 85).—II. Changes in [H⁺] of mixtures of NaNO₂ with NHPHMe, *p*-*o*-C₆H₄Me·NH·CH₂Ph, or NH₂Ph and varying amounts of HCl in MeOH are measured. For the *sec*-amines, a slight increase in [H⁺] is followed by a very rapid one. Formation of diazo-compounds with NH₂Ph probably masks a similar initial change. The changes are in line with those in conductivity.

III. The nitrites of *p*-C₆H₄X·NH₂ (X = Me, OEt, and Cl) are isolated. When kept at 0°, they give 71.5, 62.7, and 80% of diazoamino- (*A*) with 21.7, 22.9, and 4.6%, respectively, of sol. diazo-compound (*B*); in H₂O at 20° they give 65, 61.9, and 72.8% of (*A*) with 23.8, 25.4, and 7.4%, respectively, of (*B*). NH₂Ph·HNO₂ is also isolated, but β-C₁₀H₇·NH₂·HNO₂ is too unstable. The nitrites of NHPHMe and *p*-C₆H₄Me·NHMe are isolated and, when kept, give *N*-NO-derivatives. Decomp. of *p*-C₆H₄Me·NHR·HNO₂ (R = H or Me) in MeOH at 25° appears to be a second-order reaction, but the mechanism is still uncertain.

R. S. C.

Cleavage of phenylbenzyltrimethylammonium chloride by sulphur-containing salts. H. R. SNYDER and J. C. SPECK (J. Amer. Chem. Soc., 1939, 61, 668—670).—CH₂Ph·NPhMe₂Cl (I) is cleaved by

boiling aq. NaHSO_3 , Na_2SO_3 , NaHS , Na_2S , $\text{Na}_2\text{S}_2\text{O}_3$, or KSCN (cf. aneurin), but not by NaCN , NaOPh , NaBO_3 , NaOH , or Na_3PO_3 . In the cold, KSCN gives *phenylbenzylidimethylammonium thiocyanate*, m.p. 104° , which in boiling H_2O yields $\text{CH}_2\text{Ph}\cdot\text{SCN}$ (60%) and NPhMe_2 (68%). With NaHSO_3 , SO_2 is evolved (owing to the HCl liberated) and NPhMe_2 (24%) and $\text{CH}_2\text{Ph}\cdot\text{SO}_3\text{Na}$ are formed; Na_2SO_3 gives 63% of NPhMe_2 and 82% of $\text{CH}_2\text{Ph}\cdot\text{SO}_3\text{Na}$, and, in accordance with these higher yields, the reaction with NaHSO_3 gives better results if an excess of NaHSO_3 is used. NaHS gives NPhMe_2 (82%), $\text{CH}_2\text{Ph}\cdot\text{SH}$ (18%), and $(\text{CH}_2\text{Ph})_2\text{S}$ [54%, formed from $\text{CH}_2\text{Ph}\cdot\text{SH}$ and unchanged (I)]. Na_2S gives NPhMe_2 (68%) and $(\text{CH}_2\text{Ph})_2\text{S}$ (75%). With $\text{Na}_2\text{S}_2\text{O}_3$, the $\text{CH}_2\text{Ph}\cdot\text{S}_2\text{O}_3\text{Na}$ primarily formed also reacts with more (I), yielding *phenylbenzylidimethylammonium S-benzyl thiosulphate* (94%), m.p. 104° . Na_2SO_3 and NaHSO_3 react more slowly than do the other salts. R. S. C.

Molecular dissymmetry due to restricted rotation in the benzene series. An optically active ethylenic derivative. W. H. MILLS and G. H. DAZELEY (J.C.S., 1939, 460—463).— $o\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (I) (prep. from $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ and Me_2SO_4 at 100°), b.p. $137\text{—}142^\circ/17\text{ mm.}$, and MgPr^2Cl give *o-dimethylaminophenyldiisopropylcarbinol*, m.p. 66° , dehydrated by boiling Ac_2O to *o-dimethylamino- β - β -dimethyl- α -isopropylstyrene*, b.p. $127\text{—}132^\circ/15\text{ mm.}$ (perchlorate). This gives successively a methosulphate, methopicate, and methiodide (II), m.p. 160° ; (II) yields the *d*-bromocamphorsulphonates, $[M]_{5461}^{20} +288^\circ$ and $+394^\circ$ in H_2O , and thence the *l*- and *d*-iodides, m.p. 160° , $[M]_{5461}^{20} -58^\circ$ and $+55^\circ$ in H_2O , respectively. The iodides are stable ($\leq 97\%$) in H_2O at 100° for 8 hr. MgEtBr and (I) give similarly *o-dimethylaminophenyldiethylcarbinol*, an oil (perchlorate), and thence *o-dimethylamino- β -methyl- α -ethylstyrene*, b.p. $117\text{—}122^\circ/18\text{ mm.}$ (picrate), and its methopicate and methiodide, m.p. 157° ; this compound was insoluble, presumably because of the insufficient overlap of the substituent groups [$\beta\text{-H}$, whereas (II) has $\beta\text{-Me}$]. R. S. C.

Organic compounds in chemotherapy. I. Derivatives of sulphanilamide. II. Preparation of formaldehydesulphoxylate derivatives of sulphanilamide and amino-compounds. H. BAUER (J. Amer. Chem. Soc., 1939, 61, 613—616, 617—618).—I. By condensing $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ with the appropriate base in presence of an excess of the base or the alkali named in parentheses, are prepared *N-N'-acetylsulphanilylsulphanilyl-sulphanilamide* (NaHCO_3), m.p. 268° , *-amidoethyl alcohol* (NaHCO_3), m.p. 153° , and *-glycine* (NaOH), m.p. 247° , *N-acetylsulphanilyl-sulphanilamide*, m.p. 274° , *-amidoethyl alcohol*, m.p. 156° , *-glycine* (NaOH), m.p. 237° , *-p-carboxyanilide* ($\text{C}_5\text{H}_5\text{N}$), m.p. 252° , and *-p-nitroanilide* ($\text{C}_5\text{H}_5\text{N}$), m.p. 264° . Hydrolysis, usually by 5N-HCl , then yields *N-sulphanilyl-sulphanilamide*, m.p. 137° (Na salt), *-amidoethyl alcohol*, m.p. 101° , *-glycine*, m.p. 154° , *-p-carboxyanilide*, m.p. (anhyd.) 202° , (+ EtOH) 196° , and *-p-nitroanilide*, m.p. 165° (reduced to the NH_2 -anilide, m.p. 138°), *N-N'-sulphanilylsulphanilyl-sulphanilamide*, m.p.

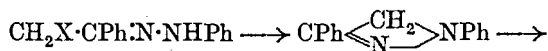
209° , *-amidoethyl alcohol*, m.p. 144° , and *-glycine*, m.p. 188° . The chemotherapeutic activity of several of the products exceeds that of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (I).

II. Addition of (I) and $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{Na}$ to AcOH gives *Na sulphanilamideformaldehydesulphoxylate*, $+2\text{H}_2\text{O}$, which is less active than (I). Na_2 4:4'-diaminodiphenylsulphonebisformaldehydesulphoxylate, $+2\text{H}_2\text{O}$, similarly prepared, is less active and less toxic than the sulphone, but the corresponding Na_2 bisformaldehydebisulphite, $+4\text{H}_2\text{O}$, has very little activity. R. S. C.

1:3-Diaminocyclohexane. A. SKITA and R. RÖSSLER (Ber., 1939, 72, [B], 461—468).— Me_2 *cis*-hexahydroisophthalate is converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ into *cis-hexahydroisophthaldihydrazide* (I), m.p. 265° (decomp.) (diisopropylidene derivative, m.p. 239°). Similarly Me_2 *trans*-hexahydroisophthalate affords *trans-hexahydroisophthaldihydrazide* (II), m.p. 130° (diisopropylidene derivative, m.p. 211°). Directions are given for the isolation of (I) and (II) from the product of the action of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ on a mixture of the isophthalates. (I) is converted by NaNO_2 and HCl into the explosive azide and thence by EtOH into *hexahydrophenylene-1:3-diurethane* (III), m.p. $149\text{—}5^\circ$, also obtained from (II) through the very unstable azide; a *by-product*, $(\text{C}_8\text{H}_{11}\text{O}_2\text{N})_2$, m.p. 190° , is also obtained. (III) is hydrolysed by cone. HCl at $100\text{—}120^\circ$ to 1:3-diaminocyclohexane (IV), b.p. $198^\circ/760\text{ mm.}$ (monohydrochloride; picrate, m.p. 265°). Partial hydrogenation (Pt-BaSO_4 in $\text{HCl-H}_2\text{O-AcOH}$) of $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ gives $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$. If an aged catalyst is used the rate of reaction is diminished, but complete hydrogenation at 60° gives (IV) and small amounts of an isomeric base, b.p. $202\text{—}204^\circ$ (picrate, decomp. 254°). (IV) is probably the *cis*-modification and richer in energy since it is formed exclusively if the hydrogenation is rapid. H. W.

Preparation of mixed azoxy-compounds by the action of nitroso-compounds on β -aryl-hydroxylamines. V. O. LUKASCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1938, 21, 376—379; cf. A., 1938, II, 481).— $\text{NHAr}\cdot\text{OH}$ and NO -compounds with dissimilar radicals give not only sym., but mixed, azoxy-compounds (cf. Bamberger, *et al.*, A., 1898, i, 20). The relative yields vary with the rates of azoxy-coupling and also the process: $\text{RNO} + \text{NHR}'\cdot\text{OH} \rightleftharpoons \text{R}'\text{NO} + \text{NHR}\cdot\text{OH}$. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{OH}$ and PhNO in EtOH at $0\text{—}5^\circ$ or 25° , or $\text{NPh}\cdot\text{OH}$ and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}$, give mixtures of azoxybenzene and its 4-Cl-, m.p. $61\text{—}62^\circ$, and 4:4'-Cl₂-derivatives. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{OH}$ gives 4:4'-dibromo- and isomeric 4-bromo-azoxybenzenes, m.p. $92\text{—}93^\circ$ and $71\text{—}72^\circ$. Other mixed derivatives described are: 2-, new m.p. $127\text{—}128^\circ$, 3-, m.p. $184\text{—}185^\circ$, and 4-CO₂H- (β -form; Angeli); 4'-chloro-3-carboxy-, m.p. $258\text{—}259^\circ$; 3-carboxy-2', m.p. $162\text{—}163^\circ$ (NH_4 salt, m.p. $176\text{—}176\cdot5^\circ$) (an isomeride has m.p. $142\text{—}143^\circ$), -3', m.p. $188\text{—}189^\circ$, and -4'-methyl-, m.p. $209\text{—}210^\circ$, 2-carboxy-2'-methyl-azoxybenzene, m.p. $150\text{—}152^\circ$. 3-Carboxy-4'-methylazobenzene, new m.p. $209\cdot5\text{—}210^\circ$, and analogous derivatives are described. A. T. P.

"Tetraphenyltetracarbazone." II. Action of phenylhydrazine on ω -halogeno-ketones. S. BODFORSS (Ber., 1939, 72, [B], 468-482; cf. A., 1920, i, 96).—Ebullioscopic and cryoscopic determinations of the mol. wt. of the compound (I) obtained from CH_2BzCl and $\text{NHPh}\cdot\text{NH}_2$ indicate moderate association. Comparison of the absorption spectra of (I) in EtOH or hexane with that of Et benzeneazocrotonate indicates the probability that (I) is an azo-compound (not 1:3-diphenyl- Δ^2 -1:2-diazone as considered previously), the indefiniteness of the benzeneazo-band being probably due to the association of (I) or to peculiarities in the nature of the conjugated linking. There is no similarity in the behaviour of (I) and $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$. Since the optical behaviour affords no evidence against the azo-constitution, (I) is now regarded as α -phenylvinylphenyldi-imide [α -benzeneazo- α -phenylethylene], $\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NPh}$. It is very resistant to oxidation, is unaffected by OsO_4 , AcCl or BzCl in $\text{C}_6\text{H}_5\text{N}$, or according to Schotten-Baumann. PhNCO reacts slowly and in a non-elucidated manner with (I) giving the substance, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_4$, m.p. 211° . Reduction of (I) by Na-Hg in EtOH affords diphenacyldiphenylhydrazone (II), m.p. 195° (slight decomp.), also obtained from $\text{NHPh}\cdot\text{NH}_2$ and (I) at 120° or from CH_2BzBr and $\text{NHPh}\cdot\text{NH}_2$ in hot EtOH. If $\text{NHPh}\cdot\text{NHMe}$ is used in place of $\text{NHPh}\cdot\text{NH}_2$ there is evolution of H_2 without formation of cryst. products. With hot NH_3Ph there is evolution of gas without production of solids. The tetraphenyl- β -tetracarbazone of Scholtz (A., 1919, i, 95), regarded by Bodforss (*loc. cit.*) as 1:4-dianilino-2:5- (or -2:6-) diphenylpyrazine, is shown to be (II). (I) reacts very readily with Br in AcOH containing KOAc without yielding characteristic products. It does not react with $\text{Na}_2\text{S}_2\text{O}_4$, CH_2O , $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, N_2H_4 , $\text{CH}_2(\text{CO}_2\text{Et})_2$, or $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ in NaOEt-EtOH , HCN in AcOH , H_2O , CHCl_3 and alkali, or amyl nitrite in EtOH or AcOH . Measurements of the rate of change of electrical conductivity and extinction during the reaction show the course to be:



$\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NPh}$. $\text{NHPh}\cdot\text{NH}_2$ reacts at about the same rate with CH_2BzI as with CH_2BzBr , less readily with CH_2BzCl , and still less readily with $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$; qualitatively the sequence is the same as that observed in the reaction between halogenoketones and NaOEt in EtOH. Desyl chloride reacts more slowly and appears to yield exclusively β -benzildiphenylhydrazone. In an anomalous reaction $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ and CH_2BzBr yield phenylglyoxaldi- p -nitrophenylhydrazone, m.p. $>270^\circ$. CH_2BzBr and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}_2$ give α -phenylvinyl- o -tolyl-di-imide, m.p. 160° (decomp.). $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NH}_2$ give two isomeric compounds, $\text{C}_{16}\text{H}_{16}\text{ON}_2$, m.p. 80° and 134° . α -*Anisylvinyl- o -tolyl-di-imide* has m.p. $\sim 80^\circ$ (decomp.). H. W.

Diazo-chemistry. H. H. HODGSON (Rec. trav. chim., 1939, 58, 306-307).—Controversial with Schoutissen (cf. A., 1938, II, 318). A. T. P.

Tetrazotisation of o -phenylenediamine. H. A. J. SCHOUTISSEN (Rec. trav. chim., 1939, 58, 308-310).—A reply to Hodgson (preceding abstract).

A. T. P.

Behaviour of phenols in presence of amines.—See A., 1939, I, 264.

Exchange of hydrogen atoms between nitrophenols and water. III.—See A., 1939, I, 269.

Reactions with amyl nitrite. I, II. T. AJELLO and G. SIGILLÒ (Gazzetta, 1939, 69, 57-65, 65-72).—I. Excess of $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$ in Et_2O with $\text{COR}\cdot\text{CH}_2\text{R}'$ gives $\text{COR}\cdot\text{CR}'\cdot\text{N}\cdot\text{OH}$. Thus COMeEt gives $\text{COMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ gives $\text{COMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{OH}$, and $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ gives $\text{COPh}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{OH}$. $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ and $(\text{CH}_2\text{Bz})_2$ do not react. COPhMe gives BzOH .

II. Under similar conditions PhOH gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$; o - and m -cresol give 3:5:1:2- $(\text{NO}_2)_2\text{C}_6\text{H}_2\text{Me}\cdot\text{OH}$ and 6:1:3- $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}\cdot\text{OH}$; o -, m -, and $p\text{-C}_6\text{H}_4(\text{OH})_2$ give respectively 3:1:2+4:1:2- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, 4:1:3- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})_2$, and quinhydrone + $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$; $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ gives 3:5:1:2- $(\text{NO}_2)_2\text{C}_6\text{H}_2(\text{OMe})\cdot\text{OH}$; 1:3:5- and 1:2:3- $\text{C}_6\text{H}_3(\text{OH})_3$ give unidentified NO_2 -derivatives; thymol gives 6:1:4:3- $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{MePr}^{\beta}\cdot\text{OH}$; $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ gives its 1- NO_2 - and 1:8- $(\text{NO}_2)_2$ -derivatives, and $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{OH}$ gives $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.

E. W. W.

Hardening process of phenol-formaldehyde resins. A. ZINKE, F. HANUS, and E. ZIEGLER [with F. SPERK, H. TROGER, and E. WEINHARDT] (J. pr. Chem., 1939, [ii], 152, 126-144).—The products of the acidic condensation of phenols with CH_2O are probably mixtures of phenols of polyphenylpolymethylene compounds. They cannot be hardened directly owing to the absence of alcoholic groups. By fresh, alkaline condensation with CH_2O they pass into alcohols of the polyhydroxyphenylpolymethylene series which can be hardened. The hardenable resins are phenolic alcohols and alcohols of the dihydroxydiphenylmethane series. The hardening process commences at a temp. somewhat above the m.p. and at first involves mainly evolution of H_2O . Only at a much higher temp. is CH_2O evolved in quantity. The amount of H_2O evolved is ~ 1 mol. and much exceeds that of CH_2O . Elimination of H_2O occurs with production of O-bridges and probably does not involve a phenolic OH since it takes place with equal readiness if OH is replaced by $\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$. Evolution of CH_2O takes place only when a phenolic OH is free. o -Cresol, CH_2O , and NaOH at room temp. yield 4:4'-dihydroxy-3:3'-dimethyl-5:5'-dihydroxymethyldiphenylmethane, m.p. 155° (tetra-acetate, m.p. 77°), also obtained from 4:4'-dihydroxy-3:3'-dimethyldiphenylmethane and from 2-methyl-4:6-dihydroxymethylphenol. $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, CH_2O , and 10% NaOH at room temp. or 30-40° give 2-chloro-6-hydroxymethylphenol, m.p. 115° , converted by renewed alkaline condensation with CH_2O into 5:5'-dichloro-4:4'-dihydroxy-5:5'-dihydroxymethyldiphenylmethane, m.p. 141° , also prepared from 3:3'-dichloro-4:4'-dihydroxydiphenylmethane, m.p. 103° . p -cycloHexylphenol, CH_2O , and 10% NaOH yield

4-cyclohexyl-2:6-dihydroxymethylphenol, m.p. 106—107° [*p*-toluenesulphonate (I), m.p. 162—162.5°]. 4-Phenyl, m.p. 110—111.5° (softening at 108°), and 4-tert.-amyl-, m.p. 48°, 2:6-dihydroxymethylphenol are described. The *p*-toluenesulphonate, m.p. 134°, of di(hydroxymethyl)quinol Me ether (II) is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to 2:6-dialdehydoquinol Me ether *p*-toluenesulphonate, m.p. 121.5° (dioxime, m.p. 158°), hydrolysed to 2:6-dialdehydoquinol Me ether, m.p. 138° (dioxime, m.p. 190°); this is obtained directly when (II) is heated at 160° in CO_2 . Hydroxyuvitic dialdehyde, m.p. 131°, is obtained as by-product of the resinification of di(hydroxymethyl)-*p*-cresol (III). (I) is oxidised to the *p*-toluenesulphonate, m.p. 133°, of 2:6-dialdehydo-4-cyclohexylphenol, m.p. 113°. The *p*-toluenesulphonate, m.p. 151°, of di(hydroxymethyl)-*p*-chlorophenol (IV) is oxidised to the *p*-toluenesulphonate, m.p. 123°, of 4-chloro-2:6-dialdehydophenol, m.p. 126° (dioxime, m.p. 203—204°), also obtained during the resinification of (IV) at 180° in CO_2 . Extraction of the resin obtained from (III) at 140° with aq. 3% NaOH gives a sol. colourless product, m.p. ~70°, converted by HBr in AcOH into the dibromide, m.p. 114°, of (III); the alkali-insol. portion similarly affords only traces of the dibromide. H. W.

2:2-Di-*p*-hydroxyphenyldecahydronaphthalene.—See B., 1939, 356.

β -Anilino- β' -aryloxydiethyl ethers and related ethers.—See B., 1939, 356.

Sterical conditions in cyclic isopropylidene ethers of *o*-diphenols. J. BÖESEKEN (Proc. K. Akad. Wetensch. Amsterdam, 1939, 42, 240—244).—Although in aliphatic diols (I) ease of CMe_2 ether formation and increase in conductivity of H_3BO_3 [by (I)] run parallel, this is not so with *o*-diphenols (II). There is greater strain in formation of a CMe_2 ether than in formation of a complex from H_3BO_3 , and the equilibrium $(\text{II}) + \text{CMe}_2 \rightleftharpoons \text{CMe}_2\text{ether} + \text{H}_2\text{O}$ lies largely to the left. This is confirmed by comparison of the differences in heats of combustion of (I) and their CMe_2 ethers and of (II) and their CMe_2 ethers; in the latter case, the differences are much larger. J. D. R.

Structure and synthesis of croweacin. W. BAKER, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1939, 439—443).—Croweacin (I) is shown by degradation and synthesis to be 2-methoxy-3:4-methylenedioxyallylbenzene (cf. A., 1938, II, 274). Natural (I) with O_3 in MeOAc at 0° gives 2-methoxy-3:4-methylenedioxyphenylacetaldehyde (II) (isolated as semicarbazone, decomp. 194—195°; 2:4-dinitrophenylhydrazones, m.p. 169—170°), CH_2O , 2-methoxy-3:4-methylenedioxyphenylacetic acid, m.p. 118—119°, and a phenol. With KMnO_4 it gives the glycol (III), softens at 87°, m.p. 90—91° (cf. *loc. cit.*), 2-methoxy-3:4-methylenedioxybenzaldehyde, and croweacin acid (IV). KMnO_4 -aq. NaOH converts (III) into (IV), but $\text{Pb}(\text{OAc})_4$ in AcOH gives (II). Boiling KOH-EtOH isomerises natural (I) to isocroweacin (V), b.p. 145—147°/12 mm. (picrate, m.p. 75—76°), which with Br (excess) in AcOH gives 5:6:1:2:3:4- $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:OMe}$. (I) gives no picrate. 2:3:1-

$\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:OMe}$ has m.p. 41°, b.p. 112°/17 mm. 3:4:2:1- $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_2(\text{OH})\text{:CO}_2\text{H}$ (Baker *et al.*, A., 1938, II, 484) with $\text{Me}_2\text{SO}_4\text{-KOH}$ in aq. CMe_2 gives the Me ether [= (IV)]. 2-Hydroxy-3:4-methylenedioxyallylbenzene (containing some 4:2:3-isomeride) (*loc. cit.*) with $\text{Me}_2\text{SO}_4\text{-KOH-H}_2\text{O-MeOH}$ gives the impure Me ether [= (I)]; with KOH-EtOH this affords a little 4-methoxy-2:3-methylenedioxypropenylbenzene (VI), m.p. 64°, as well as (V). With Br (excess) in hot AcOH (VI) gives 5:6: $\alpha\beta$ -tetrabromo-4-methoxy-2:3-methylenedioxy-n-propylbenzene, m.p. 115°, i.e., the side-chain is not lost as with (V). KMnO_4 converts synthetic (V) and (VI) into (IV) and 2:3:4:1- $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_2(\text{OMe})\text{:CO}_2\text{H}$, respectively. Myristicin and $\text{KMnO}_4\text{-KOH}$ give "myristicin glycol" [β -dihydroxy-3-methoxy-4:5-methylenedioxypropylbenzene], m.p. 90—91°. Myristinaldehyde-2:4-dinitrophenylhydrazone has m.p. 232° after sintering. R. S. C.

Electrochemical reduction in acid solution of *p*-nitrophenetole. W. E. BRADT and A. W. ERICKSON (Trans. Electrochem. Soc., 1939, 75, Preprint 13, 139—148).—A 94% yield of *p*- $\text{NH}_2\text{:C}_6\text{H}_4\text{:OEt}$ is obtained from *p*- $\text{NO}_2\text{:C}_6\text{H}_4\text{:OEt}$ in dil. H_2SO_4 (with stirrer) and Cu gauze cathode, with Pb anode in dil. H_2SO_4 at 70° using c.d. 5 amp. per sq. dm. for 58 min. A slight increase was obtained in presence of TiO_2 , V_2O_5 , FeCl_2 , CuCl_2 , CuSO_4 , Ag_2SO_4 , AuCl_3 , and HgCl_2 whilst KBr causes a decreased yield. The effects of change of temp., current, and acid concn. are tabulated. F. R. G.

Influence of substituents on reactivities of benzene derivatives.—See A., 1939, I, 263.

Aromatic compounds of fluorine; fluorothiophenol. M. SEYHAN [with S. AKSU] (Ber., 1939, 72, [B], 594—595).—Successive treatment of *p*- $\text{C}_6\text{H}_4\text{FBr}$ with Mg and S in Et_2O gives *p*-fluorothiophenol, b.p. 162°/atm. pressure, in 26% yield. It is converted by $\text{K}_3\text{Fe}(\text{CN})_6$ into the non-cryst. disulphide. H. W.

Action of alkali on aryl thiosulphates. A. DURNOW (Ber., 1939, 72, [B], 568—570; cf. Baumgarten, A., 1930, 1029).—The decomp. of aryl thiosulphates by alkali occurs according to the scheme: $\text{SPh}_2\text{SO}_3\text{K} + \text{KOH} = \text{SPh}_2\text{OH} \text{ (I)} + \text{K}_2\text{SO}_3$; $2(\text{I}) + \text{KOH} = \text{PhSH} \text{ (II)} + \text{PhSO}_2\text{H} + \text{H}_2\text{O}$; $(\text{I}) + (\text{II}) = \text{Ph}_2\text{S}_2 + \text{H}_2\text{O}$. Pyridinium β -naphthyl thiosulphate (III), m.p. 162°, and aq. KOH at room temp. give (β - C_{10}H_7) $_2\text{S}_2$ and β - $\text{C}_{10}\text{H}_7\text{:SO}_2\text{H}$, m.p. 105—106°. (III) is converted by the requisite alkali or base into the corresponding K, m.p. 260—265° (decomp.), NH_2Et , m.p. 117—118°, and NH_3Ph , m.p. 182—183°, salts. Pyridinium 1-anthraquinonyl thiosulphate, m.p. >300°, from 1-thiolanthraquinone and pyridinium-1-sulphonic acid at 180—190°, is converted by KOMe in MeOH into the K salt, m.p. >300°, which is hydrolysed by aq. KOH at 100° to 1-anthraquinonylsulphonic acid (Et ester, m.p. 147°). H. W.

Electrolytic reduction of benzoic acid to benzyl alcohol. S. SWANN, jun., and G. D. LUCKER (Trans. Electrochem. Soc., 1939, 75, Preprint II, 105—118).—Pb and Cd, but not Sn, Hg, Zn, Al, Ni, Cu, and Fe, cathodes effect reduction of BzOH (in $\text{EtOH-H}_2\text{SO}_4$).

to $\text{CH}_2\text{Ph}\cdot\text{OH}$. The best yield was obtained at extruded 99.99 + % Pb and was as good as that of Mettler (A., 1905, i, 436). The Pb cathode loses its activity after prolonged use; PbSO_4 is formed.

F. R. G.

Halogenomethylation of aromatic compounds in acetic acid. G. DARZENS (Compt. rend., 1939, 208, 818—820).—Prolonged interaction of C_6H_6 derivatives in AcOH with $(\text{CH}_2\text{O})_3$ and anhyd. HHal (1 mol.) at 100—110° affords benzyl halide (cf. A., 1936, 461). PhMe thus affords 85% of a mixture of *o*- and much *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Cl}$; higher homologues of C_6H_6 react more easily. With less reactive substances, e.g., *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, ZnCl_2 aids the reaction. The halogenomethyl derivatives are reduced (Al, HCl—EtOH) to the corresponding hydrocarbons. The AcOH is considered to react thus: $\text{CH}_2\text{O} + \text{AcOH} + \text{HCl} \rightarrow \text{CH}_2\text{Cl}\cdot\text{OAc}$.

J. L. D.

Properties of the thiomethylene radical. Behaviour with aluminium chloride in benzene. S. W. LEE and G. DOUGHERTY (J. Org. Chem., 1939, 4, 48—53).—Normal primary amyl sulphide, amyl mercaptan, and EtSH undergo little or no change when warmed with AlCl_3 and C_6H_6 at 80°. $\text{CH}_2\text{Ph}\cdot\text{SH}$ with 1 mol. of AlCl_3 in a large excess of C_6H_6 reacts mainly thus: $\text{CH}_2\text{Ph}\cdot\text{SH} + \text{C}_6\text{H}_6 + \text{AlCl}_3 = \text{CH}_2\text{Ph}_2 + \text{H}_2\text{S} + \text{AlCl}_3$; some material, b.p. >360°, is also obtained but, as this is free from S, the reaction may be regarded as one of alkylation. Under the mild conditions used $(\text{CH}_2\text{Ph})_2\text{S}$ and AlCl_3 give mainly $(\text{CH}_2\text{Ph})_3\text{SCl}$ without participation of C_6H_6 : $(\text{CH}_2\text{Ph})_2\text{S}\cdot\text{AlCl}_3$ (I) $\rightarrow \text{CH}_2\text{PhCl} + \text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{AlCl}_3$ and (I) + $\text{CH}_2\text{PhCl} \rightarrow (\text{CH}_2\text{Ph})_3\text{SCl}\cdot\text{AlCl}_3$. CH_2PhCl and $(\text{CH}_2\text{Ph})_2\text{S}$ do not ordinarily yield a sulphonium salt and it is probable that the AlCl_3 not involved in the fission accelerates the production of the salt and forms with it a 1 : 1 additive product. If an excess of AlCl_3 is employed the main product is CH_2Ph_2 and the amounts of $(\text{CH}_2\text{Ph})_3\text{SCl}$ and $\text{CH}_2\text{Ph}\cdot\text{SH}$ are correspondingly less. Trimethylene trisulphide (II) and AlCl_3 in the ratios 4 : 3, 1 : 1, and 2 : 3 scarcely involve C_6H_6 in their interaction, the products resulting after decomp. with H_2O being S and $(\text{CH}_2\text{S})_3\cdot\text{MeCl}$. With (II) and AlCl_3 in the ratio 1 : 2 or 1 : 3 the main products are CH_2Ph_2 and $(\text{CH}_2\text{Ph})_2\text{S}$. The results may be explained by assuming that the normal additive compound is $(\text{CH}_2\text{S})_3\cdot 2\text{AlCl}_3$ and that this ratio must be exceeded and at least a slight excess of AlCl_3 be present before the C_6H_6 can become activated and take part in the reaction. The mol. of (II) then breaks and there is an addition of 2 mols. of C_6H_6 thus: $(\text{CH}_2\text{S})_3\cdot 2\text{AlCl}_3 + 4\text{C}_6\text{H}_6 + \text{trace or more of AlCl}_3 \rightarrow (\text{CH}_2\text{Ph})_2\text{S}\cdot\text{AlCl}_3 \rightarrow \text{CH}_2\text{Ph}_2 + 2\text{H}_2\text{S} + \text{AlCl}_3$.

H. W.

β -2 : 4 : 6-Trinitrophenoxyethyl nitrate.—See B., 1939, 443.

Metal ketyls ; reaction with keto-groups. R. OPPENAUER (Rec. trav. chim., 1939, 58, 316—328).—Benzpinacol, $\text{Et}_2\text{O}\cdot\text{MgEtBr}$, and C_6H_6 at 40—45°, then $\text{C}_5\text{H}_5\text{N}$ (whereby a ppt., $\text{MgBr}_2\cdot 3\text{C}_5\text{H}_5\text{N}$, is formed), give ultimately a blue solution (A) which with $\text{PhCHO}\cdot\text{C}_6\text{H}_6$ at 50—55°, affords triphenyl-ethylene glycol (I), m.p. 165—166° (94% yield).

$\text{Hg}\cdot\text{Mg}$ (or Na) and COPh_2 in $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ for 3 (or 2) days (no $\text{C}_5\text{H}_5\text{N}$), followed by $\text{PhCHO}\cdot\text{C}_6\text{H}_6$, also give (I) in lower yield. *p*- $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (II) and (A) at 45° afford α -diphenyl- β -*p*-benzoyloxyphenyl-ethylene glycol, m.p. 208—210° [decomp. by $\text{Pb}(\text{OAc})_4$ in C_6H_6 to COPh_2 and (II)], hydrolysed ($\text{KOH}\cdot\text{EtOH}$) to α -diphenyl- β -*p*-hydroxyphenylethylene glycol, m.p. 183—184°. Use of $\text{MgEt}(\text{Br}, \text{Cl})$ without $\text{C}_5\text{H}_5\text{N}$ gives lower yields. cycloHexanone and (A) (prep. with MgEtI) afford 1-hydroxy-1- α -hydroxy-benzhydrylcyclohexane, m.p. 129.5—130.5°, also obtained from Et cyclohexan-1-ol-1-carboxylate and MgPhBr . Anthrone pinacol with $\text{MgEtBr}\cdot\text{C}_6\text{H}_6\cdot\text{C}_5\text{H}_5\text{N}$ and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (III) give 9-hydroxy-9-*p*-dimethylamino- α -hydroxybenzyl-9 : 10-dihydro-anthracene, m.p. 150—152° [$\text{CrO}_3\cdot\text{AcOH}$ gives anthrone and (III)]. Xanthone pinacol and PhCHO similarly give 9-hydroxy-9- α -hydroxybenzylxanthone, m.p. 192—195° [$\text{Pb}(\text{OAc})_4$ in C_6H_6 gives xanthone and PhCHO]. The pinacol from Michler's ketone (IV) and (II) give (after hydrolysis with $\text{EtOH}\cdot\text{KOH}$) α -di-(*p*-dimethylaminophenyl)- β -*p*-hydroxyphenylethylene glycol, m.p. 154—156° [$\text{Pb}(\text{OAc})_4\cdot\text{MeOH}$ gives (IV) and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$]. The mechanism of the general reaction is discussed. All operations involving the ketyls are carried out in N_2 and m.p. are corr.

A. T. P.

2 : 2 : 5-Trimethylcyclohexane-1 : 3-diol and its dehydration product. V. P. HIRSJÄRVI (Suomen Kem., 1939, 12, B, 3—4).—Reduction (method: Zelinski *et al.*, A., 1913, i, 607) of 2 : 5 : 5-trimethylcyclohexane-1 : 3-dione gives 2 : 5 : 5-trimethylcyclohexane-1 : 3-diol (I), m.p. 116.5—117°, and hexan-1-ol, b.p. 86—89°/18 mm. (I) is dehydrated by KHSO_4 at 300° to 1 : 1 : 4-trimethyl- Δ^3 -cyclohexadiene (II), b.p. 130—135°/770.4 mm., which is oxidised by alkaline KMnO_4 at < -4° to the lactonic acid, $\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{H}$, m.p. 192.5—194.5°, converted by AgNO_3 into α -dimethylsuccinic acid (III) [also formed with AcOH and $\text{H}_2\text{C}_2\text{O}_4$ from (II) and KMnO_4 at 8°]. Ozonisation of (II) in EtOAc, followed by Zn reduction (not colloidal Pd), gives neutral and acidic CHO-derivatives; the last is oxidised (KMnO_4) to (III). Elimination of 1 mol. of H_2O from (I) affords 2 : 5 : 5-trimethyl- Δ^3 -cyclohexenol, b.p. 72.5—74.5°/7 mm., also oxidised to (III).

A. T. P.

Hydrolysis of triphenylmethyl chloride in dioxan. D. R. READ and W. TAYLOR (J.C.S., 1939, 478—484).—Below certain concns., the reaction, $\text{CPh}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{CPh}_3\cdot\text{OH} + \text{HCl}$, in dioxan is bimol. and thus follows the S_m mechanism of Taylor (A., 1938, II, 37). At higher concns. both reactants act catalytically, CPh_3Cl (0.2 g.-mol. per l.) more so than H_2O (>0.5 g.-mol. per l.), which invalidates all explanations except that excess reagents (above the max. necessary for the application of the law of mass action) may act as solvents. The reverse reaction is too fast for measurement by the method used, but the equilibrium consts. show the reaction to be truly reversible.

R. S. C.

Physical-chemical properties of cholesterol exposed to ultra-violet radiation. N. P. JERE-

MENKO (Arch. sci. biol. U.S.S.R., 1935, 37, 509—512).—Irradiation of cholesterol by unfiltered ultra-violet light induced a photochemical reaction with possible production of hydroxycholesterol. Filtered (336 mm.) light did not produce this effect.

CH. ABS. (p)

Hydrogenation of ergosterone. A. WINDAUS and K. BUCHHOLZ (Ber., 1939, 72, [B], 597—599).—Hydrogenation of ergosterone according to Marker *et al.* (A., 1937, II, 496) gives the additive product (A), m.p. 196°, which, contrary to Heilbron *et al.* (A., 1938, II, 321), is composed of equal parts of ergosterol (I) and *epialloergosterol* (II). Addition of digitonin to the filtrate from (A) ppts. the digitonides of (I) and *alloergosterol* (III) whilst (II) and *epi-ergosterol* remain in solution. The mixture of (I) and (III) is transformed into the 3:5-dinitrobenzoates, which are partly separated from one another by crystallisation from COMe_2 . Hydrolysis followed by chromatographic analysis of the product leads to the isolation of (III), m.p. 129—130°, $[\alpha]_D^{25}$ —35.96° in CHCl_3 (acetate, m.p. 137°, $[\alpha]_D^{25}$ —77.5° in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 165°, $[\alpha]_D^{25}$ —97.3° in CHCl_3). In boiling MeOH containing a little conc. HCl (III) passes into the *hydrocarbon*, m.p. 86.5°, $[\alpha]_D^{25}$ +285.7° in CHCl_3 , also obtained from (II) by this method or by treatment with NaOEt at 180°. H. W.

Sterols. L. Isolation of caoutchicol. R. E. MARKER and E. L. WITTLE (J. Amer. Chem. Soc., 1939, 61, 585—586).—The non-saponifiable part of the COMe_2 extract of a crude rubber, "jelutong," yields a trace of digitonide and, from the residue, *caoutchicol*, $\text{C}_{30}\text{H}_{50}\text{O}$, m.p. 205—210° (decomp.) [dibromide, m.p. 186—190° (decomp.)], as the *acetate*, m.p. 216° [dibromide, m.p. 225° (decomp.)], which is hydrogenated (PtO_2) in AcOH at 70°/3 atm. to *dihydrocaoutchicol acetate*, m.p. 247°. Hydrolysis then gives *dihydrocaoutchicol*, m.p. 188°, converted by CrO_3 into *dihydrocaoutchicone*, m.p. 210° [semicarbazone, m.p. 249—250° (decomp.)]. R. S. C.

Estriadiol alkyl carbonates.—See B., 1939, 437.

Separated auxo-enoid systems. VIII. Colour of p-nitrophenylacetarylamides. IX. Colour of β-p-nitrophenylpropionarylamides. V. A. ISMAILSKI and E. A. SMIRNOV (Compt. rend. Acad. Sci. U.R.S.S., 1938, 20, 669—673, 675—679).—VIII. p-Nitrophenylacet-p'-aniside, m.p. 189°, and -p'-hydroxyanilide, m.p. 233°, are almost colourless, but the -p'-dimethylaminoanilide, m.p. 217°, is reddish-orange. (Cf. A., 1937, II, 96.)

IX. β-p-Nitrophenylpropion-p'-aniside, m.p. 183°, is almost colourless, but the -p'-hydroxy-, m.p. 181°, and -p'-dimethylaminoanilide, m.p. 225.5°, are pale yellow and reddish-orange, respectively. The authors' previous theories are modified to include the colours of these six compounds. R. S. C.

Synthesis of α-naphthylacetic acid. A. CAMBRON (Canad. J. Res., 1939, 17, B, 10—13).—Paraformaldehyde, C_{10}H_8 , and conc. HCl in AcOH- H_3PO_4 at 98—100° give 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Cl}$, b.p. 145—160°/6—8 mm., converted by KCN in aq. EtOH into 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{CN}$, which is hydrolysed by aq.

$\text{H}_2\text{SO}_4\text{--AcOH}$ to α- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (over-all yield 35%). J. D. R.

Synthesis of α-naphthylacetic acid and homologues. R. H. F. MANSKE and A. E. LEDINGHAM (Canad. J. Res., 1939, 17, B, 14—22).—Crude 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Cl}$ (I) (Cambron, *supra*) contains 1:5- $\text{C}_{10}\text{H}_6(\text{CH}_2\text{Cl})_2$, b.p. 175—185°/12 mm., m.p. 144°, which with KCN in aq. dioxan gives 1:5- $\text{C}_{10}\text{H}_6(\text{CH}_2\text{CN})_2$, b.p. 230°/2 mm., m.p. 140° [hydrolysed by aq. $\text{H}_2\text{SO}_4\text{--AcOH}$ to 1:5- $\text{C}_{10}\text{H}_6(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, m.p. 280°], and a small quantity of 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{OH}$, b.p. 143—145°/2 mm., m.p. 64°, also formed by hydrolysis of α-naphthylcarbinyl acetate, b.p. 134—136°/1.5 mm. [from (I) and KOAc in AcOH]. (I) with NaCN in aq. MeOH yields 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CN}$ (II), 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{OMe}$, b.p. 101—103°/5 mm. (picrate, m.p. 95°), di-1-naphthylmethyl ether, b.p. 175—185°/1.5 mm., m.p. 121°, and α- $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{NH}_2$, m.p. 184°. Hydrolysis of (II) with aq. $\text{H}_2\text{SO}_4\text{--AcOH}$ yields α- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and a substance, $\text{C}_{23}\text{H}_{24}\text{O}_2$, m.p. 179°. γ-(1-Naphthyl)propanol with HBr yields the bromide (III), b.p. 153—155°/3 mm., which with $\text{CHNa}(\text{CO}_2\text{Et})_2$, followed by hydrolysis (EtOH--KOH) and decarboxylation, yields δ-(1-naphthyl)-valeric acid, m.p. 89° (Me ester, b.p. 153—155°/3 mm.). Me γ-(1-naphthyl)butyrate, b.p. 152—155°/0.5 mm., reduced with Na-EtOH yields δ-(1-naphthyl)-butanol, b.p. 150—155°/0.5 mm., converted [as for (III)] into the bromide, b.p. 160—163°/2 mm., which affords [as (III)] ε-(1-naphthyl)hexoic acid, m.p. 62°. M.p. are corr. J. D. R.

Synthesis of six isomeric $\text{C}_{22}\text{H}_{20}\text{O}_2$ acids. E. BERGMANN (J. Org. Chem., 1939, 4, 1—13; cf. A., 1938, II, 282).—Addition of $\text{o-C}_6\text{H}_4\text{EtBz}$ to MgPhBr gives small amounts of the *pinacol*, $\text{C}_{30}\text{H}_{30}\text{O}_2$, m.p. 151—152°, and non-cryst. $\text{o-C}_6\text{H}_4\text{Et}\cdot\text{CPh}_2\text{OH}$, converted by HCl and AcCl in C_6H_6 into the corresponding chloride, which under the successive action of Na and CO_2 affords *o-ethyltriphenylacetic acid*, m.p. 204—205° (slight decomp.). CHPh_2Br and $\text{CH}_2\text{Ph}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ at room temp. yield *Et*₂ benzylbenzhydrylmalonate, b.p. 190°/0.02 mm., hydrolysed (KOH in boiling amyl alcohol) and decarboxylated to β-phenyl-α-benzhydrylpropionic acid, m.p. 175—177°. $\text{o-C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{Et}$, m.p. 59—61.5°, is transformed by MgMeI into *o-α-phenylvinylbenzoic acid*, m.p. 136—136.5°, and α-phenyl-α-methylphthalide, m.p. 78—81°; the former substance is hydrogenated (Pd--BaSO_4 in boiling PrOH) and the latter is reduced (Zn--Cu in boiling EtOH--aq. NH_3 or red P-HI) to *o-α-phenylethylbenzoic acid* (I), m.p. 104—106°. The chloride of (I) and $\text{C}_6\text{H}_6\text{--AlCl}_3$ give only the autocondensation products, anthraquinone and 10:10'-diketo-9:9'-dimethyl-9:9':10:10'-tetrahydro-9:9'-dianthryl, m.p. 280—283° (in a sealed tube) after becoming discoloured at 258°. When heated in H_2 at 205—210° until evolution of CO_2 ceases (I) and $\text{Pb}(\text{CNS})_2$ give *o-α-phenylethylbenzonitrile*, b.p. 166—168°/5.5 mm., 151°/1.8 mm., which is transformed by MgPhBr into *o-α-phenylethylbenzophenone*, b.p. 184—186°/0.8 mm. This is converted by Na powder followed by H_2O or by Al-Hg in boiling $\text{EtOH--H}_2\text{O}$ into *o-α-phenylethylbenzhydrol*, two forms, crystals, m.p. 91—93°, or a liquid, b.p. 178—180°/0.5

mm. Methylation of these gives the *Me ethers*, b.p. 168—172°/0.8 mm., and 171—173°/0.9 mm., the configuration of which is doubtful; either ether with Na followed by CO₂ gives the same *o-α-phenylethyl*diphenylacetic acid, m.p. 140—141°, and *o-α'-carboxybenzyl-α-diphenylpropionic acid*, m.p. 261—263° (decomp.). *o-β-Phenylethylbenzoic acid* and Pb(CNS)₂ at 195° give *o-β-phenylethylbenzamide*, m.p. 128°, and *benzonitrile*, b.p. 168°/4 mm., which with MgPhBr affords *o-β-phenylethylbenzophenone*, b.p. 199—200°/3 mm. This is reduced [Al(OPrⁱ)₃ in boiling PrⁱOH] to *o-β-phenylethylbenzhydrol*, b.p. 195—196°/0.6 mm., m.p. 57° (reduction with Al-Hg in moist Et₂O gives, in addition, the *pinacol*, C₁₂H₁₈O₂, m.p. 141°), converted by HCl in boiling EtOH into *o-β-phenylethylbenzhydrol Et ether*, b.p. 200°/2.5 mm. (the *Me ether*, b.p. 177—178°/0.7 mm., is less readily obtained). With Na followed by CO₂ the ether affords *o-β-phenylethyl*diphenylacetic acid, m.p. 117.5—118.5°. CH(OEt)₃ and *o-CH₂Ph·C₆H₄·MgBr* give (no solvent) CH₂Ph₂ and *o-benzylbenzaldehyde Et₂ acetal*, b.p. 118°/0.04 mm., which is converted by dil. HCl at 120° into anthracene and *o-benzylbenzaldehyde*, b.p. 116—118°/0.03 mm. This with CH₂Ph·CO₂Na and Ac₂O at 160° gives *α-phenyl-o-benzylcinnamic acid*, m.p. 161—162°, hydrogenated (Pd-BaSO₄ in boiling PrOH) to *α-phenyl-β-o-benzylphenylpropionic acid*, m.p. 96—98°. *o-CH₂Ph·C₆H₄·CO₂H* and Pb(CNS)₂ in H₂ at 200—211° give *o-benzylbenzonitrile*, b.p. 130—133°/0.02 mm., and *o-benzylbenzamide*, m.p. 164.5°. The nitrile and MgPhBr afford *o-CH₂Ph·C₆H₄·Bz*, converted by CH₂Br·CO₂Me and Zn in C₆H₆ into (impure) *Me β-phenyl-o-benzylcinnamate*, b.p. 170°/0.005 mm. This is hydrolysed by KOH-MeOH-BuOH to *o-CH₂Ph·C₆H₄·Bz* and the stereoisomeric *β-phenyl-o-benzylcinnamic acids*, m.p. 177° (II) and 148° (III), or by KOH-EtOH to *β-hydroxy-β-β-o-benzyl*diphenylpropionic acid, m.p. 179—180° (decomp.), dehydrated by KHSO₄ at 180° to (III). Hydrogenation (Pd-BaSO₄ in boiling PrⁱOH) of (II)+(III) gives the non-cryst. *β-β-o-benzyl*diphenylpropionic acid. 2-Benzylcyclohexanol is oxidised by CrO₃ in AcOH at 80° to 2-benzylcyclohexanone, b.p. 119—121°/0.01 mm. (semicarbazone, m.p. 168—169°), which is transformed by successive treatments with Zn and CH₂Br·CO₂Me in C₆H₆ and P₂O₅ into *Me 2-benzyl-Δ¹-cyclohexenylacetate*, b.p. 135—136°/0.02 mm., m.p. 63—65°. This is converted by Pd(OH)₂-BaSO₄ at 300° into anthracene and by Br in AcOH into an ill-defined, neutral fraction, b.p. 185—190°/0.01 mm., and (?) *x-bromo-2-benzylphenylacetic acid*, m.p. 152°. H. W.

Specificity of pepsin. J. S. FRUTON and M. BERGMANN [with W. P. ANSLOW, jun.] (J. Biol. Chem., 1939, 127, 627—641).—See A., 1939, III, 518. The following have been prepared: *carbobenzyloxy-l-glutamyl-l-phenylalanine*, m.p. 162° (*Et ester*, m.p. 144°), *-d-phenylalanine*, m.p. 122° (*Et ester*, m.p. 131°), *-l-tyrosylglycine* (+H₂O), m.p. 182° (*Et ester*, m.p. 193—194°), *-l-di-iodotyrosine*, m.p. 188°, *-l-tyrosineamide*, m.p. 181°, and *-l-tyrosinehydrazide*, m.p. 194°; *carbobenzyloxyglycyl-l-glutamyl-l-tyrosine* (+H₂O), m.p. 173° (*Et₂ ester*, m.p. 169°); *carbobenzyloxy-l-glutamyl-l-phenylalanine*, m.p. 180° (*Et*

ester, m.p. 138°); *carbobenzyloxy-l-phenylalanyl-l-glutamic acid*, m.p. 180° (*Et₂ ester*, m.p. 115°); *-l-glutamyl-l-tyrosine Et ester*, m.p. 144°; *glycyl-l-glutamyl-l-tyrosine* (+2.5H₂O); *carbobenzyloxy-l-glutamyl-l-tyrosineamide*, m.p. ~240°. P. G. M.

Electrolytic preparation of 2:4-dinitrobenzoic acid from 2:4-dinitrotoluene. O. W. BROWN and A. E. BROWN (Trans. Electrochem. Soc., 1939, 75, Preprint 10, 97—104).—Using Pb electrodes and a vigorously stirred anolyte of 50% H₂SO₄ containing 2% of H₂CrO₄ and a catholyte (in porous cup) of dil. H₂SO₄ at 75±3°, c.d. 3 amp. per sq. dm., and 200% of the theoretical amount of electricity, a 73.81% yield is obtained (54.29% by chemical oxidation). The effects on the yield of varying the concn. of the anolyte, H₂CrO₄, c.d., temp. and amount of electricity used are tabulated. F. R. G.

Ammonolysis of benzyliisocyanodichloride [benzoylcarbonylamine dichloride]. J. C. AMBELANG and T. B. JOHNSON (J. Amer. Chem. Soc., 1939, 61, 632—633).—BzNCS (prep. from dry KNCS and BzCl in C₆H₆ at 110—120°), b.p. 133—137°/18 mm., gives (method: A., 1912, i, 219) NBz·CCl₂, which with NH₃ in dry Et₂O yields ONH₄·CPh·N·CN (Buddeus, A., 1890, 1253) and thence, by dil. HCl, NHBz·CN. Interaction of NBz·CCl₂ with bases thus occurs by way of NBz·CCl₂·NHR, which either loses HCl (if R = H) or reacts with more NH₂R (if R = Ar). R. S. C.

Influence of substituents on the rates of decomposition of the potassium salts of dihydroxamic acids. Lossen rearrangement. R. D. BRIGHT and C. R. HAUSER (J. Amer. Chem. Soc., 1939, 61, 618—629; cf. A., 1938, II, 14).—The rates of decomp. of 30 salts, [RCO·N·O·COR']K, are determined for 0.025M. solutions in 0.1N-aq. NH₃ (4 equivs.) at two temp. and the activation energies calc. When R = Ph, the rate α the strength of R'CO₂H, even for *o*-substituted acids. If R' = Ph and R = *m*- or *p*-substituted Ph, the rate α 1/the strength of RCO₂H. The results are in accord with electronic theories of Robinson and Ingold. RCO₂Me or RCO₂Et with NH₂OH and KOH in MeOH gives K hydroxamates, which (or as Ba salts) with R'COCl in dioxan give the following: *N-benzoyl*-, m.p. 163—164°, *-o-chlorobenzoyl*-, m.p. 130—131°, *-o-bromobenzoyl*-, m.p. 132—133°, *-o-nitrobenzoyl*-, m.p. 131—132°, *-o-toluoyl*-, m.p. 125—126°, *-m-nitrobenzoyl*-, m.p. 149—150°, *-o-anisoyl*-, m.p. 112—114°, *-phenylacetyl*-, m.p. 69—70°, *-β-phenylpropionyl*-, m.p. 99—101°, *-benzhydroxamic acid*; *N-o-chlorobenzoyl-m-chloro*-, m.p. 147°, *-m-bromo*-, m.p. 142—143°, *-p-chloro*-, m.p. 147—148°, *-p-bromo*-, m.p. 154—155°, *-o-fluoro*-, m.p. 124—125°, *-o-chloro*-, m.p. 144—145°, and *-o-bromo*-, m.p. 141—143°, *-benzhydroxamic acid*; *N-m-fluorobenzoyl-m-toluhydroxamic acid*, m.p. 114—116°; *N-benzoyl-cinnam*-, m.p. 156—157°, *-p-anis*-, m.p. 164—165°, *-p-tolu*-, m.p. 163—164°, *-hexahydrobenz*-, m.p. 148—149°, *-phenylacet*-, m.p. 121—122°, *-p-anisylacet*-, m.p. 123—124°, *-o-anisylacet*-, m.p. 116—117°, *-β-phenylpropion*-, m.p. 132—133°, *-o-tolu*-, m.p. 108—109°, *-o-anis*-, m.p. 91—92°, *-o-chlorobenz*-, m.p. 120—121°, and *-acet*-, m.p. 98—99°, *-hydroxamic acid*;

N-*o*-nitrobenzoyl-*m*-, m.p. 159—160°, -*p*-, m.p. 162—163°, and -*o*-nitrobenzhydroxamic acid, m.p. 163—164°. R. S. C.

Associating effect of the hydrogen atom. IV. Salicyl- and acetoacet-anilides. H. O. CHAPLIN and L. HUNTER (J.C.S., 1939, 484—489; cf. A., 1938, II, 404).—Salicyl- and acetoacet-anilides are shown by mol. wts. in $C_{10}H_8$ and wet m.p. to be associated in spite of the chelation between the H of the phenolic or enolic OH and the O of the amide CO. Salicyl-*o*-nitroanilide and -alkylanilides are not associated. Thus, the amide H of one mol. is probably co-ordinated with an already chelate O (phenolic or amidic) of another mol.; resonance structures are discussed. The following are incidentally described: *salicyl-methyl*-, m.p. 113°, and -*ethyl-anilide*, m.p. 78°; *Cu* salts, m.p. 212° (corr.; decomp.), 192° (corr.; decomp.), and 220° (corr.; decomp.), of acetoacet-anilide, -*m*- and -*p*-toluidide, respectively; *acetoacet-ethyl*-, m.p. 49—50° [*Na* and *Cu*, m.p. 182° (corr.), derivatives], and -*methyl-anilide*, an oil [*Na* and *Cu*, m.p. 164—165° (corr.), derivatives]. The properties of the *Cu* derivatives are those of the normal co-ordination salts of acetoacetic derivatives. R. S. C.

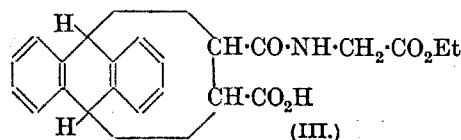
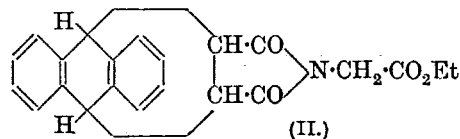
Mesomorphism and polymorphism of *p*-alkoxy-benzoic and -cinnamic acids. G. M. BENNETT and B. JONES (J.C.S., 1939, 420—425).—In each series the nematic form is found in the lower members, the tendency for existence increasing with the size of the alkyl group (up to C_5 and C_6). Later (earlier with -benzoic than -cinnamic) a smectic form appears and becomes increasingly important, i.e., as the long alkyl chain is a more important feature of the structure. Existence of a mesomorphic form of *p*-OPr- C_6H_4 -CO₂H proves that the acid is a linear dimeride of the type postulated by Sidgwick; the Me ester, as expected, shows no sign of mesomorphism. The following transition points are recorded (A = amorphous liquid; N = nematic; Sm = smectic; S = solid; M = monotropic): *p*-OR- C_6H_4 -CO₂H: R = Pr^a A-154°-N-145°-S1-116°-S2; Bu^a A-160°-N-147°-S; *n*-amyl A-151°-N-124°-S; *n*-hexyl A-153°-N-106°-S; *n*- C_7H_{15} A-148°-N-95°-Sm-92°-S2-89°-S3, S1 = M; *n*- C_8H_{17} A-148°-N-104°-Sm-100°-S2-72°-S3, S1 = M; *n*-nonyl A-141°-N-99°-Sm-92°-S2, S1 = M; *n*-decyl A-149°-N-120°-Sm-92°-S1-84°-S2; *n*-dodecyl A-137°-N-129°-Sm-95°-S2, S1 = M; cetyl A-133°-N-131°-Sm-100°-S. *trans*-p-OR- C_6H_4 -CH:CH-CO₂H: R = *n*-amyl A-176°-N-138°-S; *n*-hexyl A-182°-N-153°-S2, S1 = M; *n*-heptyl A-157°-N-150°-S; *n*-octyl A-164°-N-147°-S; *n*-nonyl A-163°-N-141°-S; *n*-decyl A-163°-N-144°-Sm-133°-S; *n*-dodecyl A-153°-N-145°-Sm-132°-S; cetyl A-158°-N-154°-Sm-132°-S (lit. m.p. 200—202°). R. S. C.

ω -Bromo-*o*-cyanostyrenes and related compounds. W. DAVIES, B. M. HOLMES, and J. F. KEFFORD (J.C.S., 1939, 357—360).—*trans*-*o*-CN- C_6H_4 -CH:CH-CO₂H and Br vapour at room temp. give *o*-CN- C_6H_4 -CHBr-CHBr-CO₂H (I), m.p. 203—204° (decomp.) (lit. 184—186°), also obtained almost quantitatively by Br in hot AcOH. *cis*-*o*-CN- C_6H_4 -CH:CH-CO₂H with a slight excess of Br

vapour gives *o*-CN- C_6H_4 -CHBr-CHBr-CO₂H (II), m.p. 154—155° (decomp.), but with a larger amount gives an unstable compound probably containing Br attached to the CN. With cold 0.02N-NaOH or boiling H₂O, (II) yields *trans*-*o*-CN- C_6H_4 -CH:CHBr (III), m.p. 86°. However, (I) is more stable; with 10—25% KOH it gives *o*-CN- C_6H_4 -CH:CHBr-CO₂H and *o*-CN- C_6H_4 -C:CH-CO₂H, but with NaOAc and steam affords 34% of *cis*-*o*-CN- C_6H_4 -CH:CHBr (IV), m.p. 30°. If (I) and (II) are not isolated, the yields of bromocyanostyrenes depend largely on the conditions of bromination; some interconversion of the cyanocinnamic acids may occur under the catalytic influence of HBr liberated. Light readily converts (IV) into a mixture containing much (III), but (III) is less easily isomerised. All the Br is removed from (IV) by boiling for 1 min. with NaOH in aq. EtOH, and *o*-CN- C_6H_4 -C:CH (4g salt) is obtained; boiling NaOH-aq. MeOH gives slowly *o*-COMe- C_6H_4 -CO₂Na and a Br-free oil. (III) is much more stable towards NaOH; in hot, aq. MeOH ω -bromostyrene-*o*-carboxylic acid, m.p. 160°, and its amide, m.p. 203—204° (obtained best by H₂O₂ and a little aq. NaOH at >86°), are formed. Both (III) and (IV), however, are relatively inert to NH₂Ph and piperidine. The spatial configurations assigned to (III) and (IV) follow analogies, but are not proved. *p*-CN- C_6H_4 -CHO, CH₂(CO₂H)₂, and a trace of piperidine in C_5H_5N give (? *trans*-)*p*-CN- C_6H_4 -CH:CH-CO₂H, m.p. 253° (lit. 248—249°), and thence by Br vapour *p*-CN- C_6H_4 -CHBr-CHBr-CO₂H, m.p. 179—182°, converted by NaOAc and steam into (? *cis*-) ω -bromo-*p*-cyanostyrene, m.p. 47.5°, which in light yields the (? *trans*-)form, softens at ~50°, m.p. 86°. Peas show only slight growth response to *cis*- and none to *trans*-*o*-CN- C_6H_4 -CH:CH-CO₂H. R. S. C.

Electrolysis of hydrindene-2-carboxylic acid. F. FICHTER and H. STENZL (Helv. Chim. Acta, 1939, 22, 425—430).—Electrolysis of hydrindene-2-carboxylic acid (I) in KOH-MeOH (Pt anode) gives (?) indene, hydrindene, 1-methoxyhydrindene, 2:2'-di-(3-methoxy-1-hydrindonyl), and 2:2'-dihydrindyl (II). (I) and H₂O₂-CHCl₃- C_5H_5N afford the peroxide, decomp. 105°, explodes on rapid heating; thermal decomp. at 200° (steel bomb) gives 20% of (II). A. T. P.

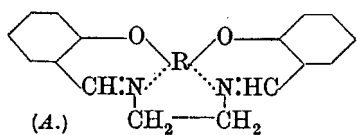
Coupling of derivatives of polycyclic hydrocarbons with glycine. W. E. BACHMANN and W. COLE (J. Org. Chem., 1939, 4, 60—67).—Anthracene-9:10-*endo*- $\alpha\beta$ -succinic anhydride (I) is converted by



NH₂-CH₂-CO₂Et in warm C_6H_6 into *Et anthracene*-9:10-*endo*- $\alpha\beta$ -succinimidoacetate (II), m.p. 187—188°,

and the acid (III), m.p. 154—156° and 175—177° after partial resolidification at 162°. (III) and CH_2N_2 yield (II). (I) and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in boiling C_6H_6 yield (II) but no (III), whilst (II) is obtained in 75% yield from (I) and $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ in $\text{C}_5\text{H}_5\text{N}$ at 100°. (II) is hydrolysed (NaOH) to *anthracene-9:10-endo- $\alpha\beta$ -succinimidoacetic acid*, m.p. 270—271°, more conveniently obtained from (I) (in $\text{C}_5\text{H}_5\text{N}$) and glycine (in aq. Na_2CO_3). Dissolution of (I) in n-NaOH followed by acidification of the solution and heating the ppt. with aq. NH_3 at 100° yields *anthracene-9:10-endo- $\alpha\beta$ -succinimide*, m.p. 303—304.5° (decomp.). 1:2-Benzanthracene-9:10-endo- $\alpha\beta$ -succinic anhydride is converted into *Et 1:2-benzanthracene-9:10-endo- $\alpha\beta$ -succinimidoacetate*, m.p. 226—227°, hydrolysed to the acid, m.p. 242—244° (decomp.). *Et 3-methylcholanthrene-6:12b-endo- $\alpha\beta$ -succinimidoacetate*, m.p. 181—182° (decomp.) (bath preheated to 170°), is obtained under strictly defined conditions and is hydrolysed to the acid, m.p. 233—234.5° (decomp.). 3-Methylcholanthrene-6:12b-endo- $\alpha\beta$ -succinimide has m.p. 252—253° (decomp.). *Et 1:2:5:6-dibenzanthracene-9:10-endo- $\alpha\beta$ -succinimidoacetate*, m.p. 220—221°, and the acid, m.p. 252—253° (decomp.), are described. H. W.

Mutual replacement of metals in internally complex salts. P. PFEIFFER, H. THIELERT, and H. GLASER (J. pr. Chem., 1939, [ii], 152, 145—156).—Internally complex salts in which R (cf. A) = Cu,



Ni, Zn, Mg, vanadyl, or ferryl are boiled in $\text{C}_6\text{H}_5\text{N}$ with various acetates (mol. ratio 1:2) and the products are worked

up by fractional crystallisation. The Cu salt is the most stable since Cu cannot be replaced by Ni, VO, FeO, Zn, or Mg, whereas the reverse replacement is very readily effected. Ni is quantitatively replaced from its salts by $\text{Cu}(\text{OAc})_2$ and, to a considerable extent by $\text{VO}(\text{OAc})_2\cdot 2.5\text{H}_2\text{O}$, particularly if an excess of the latter is used. Fe^{III} , Zn, and Mg acetates are without action on the Ni complex whilst the complexes of these three metals are quantitatively transformed by $\text{Ni}(\text{OAc})_2$ into the Ni complex. The central atom of the V complex is quantitatively replaced by Ni and Cu but not by Fe, Mg, or Zn. Conversely an excess of $\text{VO}(\text{OAc})_2\cdot 2.5\text{H}_2\text{O}$ largely replaces Fe and almost quantitatively expels Zn and Mg from their complexes. FeO has about the same stability as VO. $\text{Zn}(\text{OAc})_2$ replaces Mg from its complex whereas $\text{Mg}(\text{OAc})_2$ has no effect on the Zn salt. The complexes of Cu, Ni, V, and Fe are scarcely affected by AcOH, from which at least 90% can be recovered unchanged. On the other hand the salts of Zn and Mg are almost completely decomposed and the Schiff's base can be isolated from the solution in good yield. Conversely, good yields of the Cu, Ni, VO, and FeO salts are obtained from an excess of the Schiff's base and the metal acetate; the yields of Zn and Mg complex are 50% and 0 respectively.

H. W.

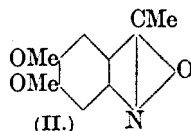
Tetracinnamoylthane. J. ŚWIDERSKI (Rocz. Chem., 1939, 19, 142—145).—Na added to dicinn-

amoylmethane in PhOMe, followed by I in Et_2O , gives *s-tetracinnamoylthane*, m.p. 230°, converted by boiling Ac_2O into 3:4-dicinnamoyl-2:5-distyrylfuran, m.p. 168°. R. T.

Fission of ketones with alkalis. II. Bromo-, methyl-, and nitro-acetophenones. G. LOCK and R. SCHRECKENEDER (Ber., 1939, 72, [B], 511—517; cf. A., 1937, II, 293).—Bromo-, methyl-, and nitro-acetophenones resemble the chloroacetophenones (*loc. cit.*) in that they are decomposed by alkali hydroxides on the aliphatic side with the formation of substituted benzoic acids; di-*o*-substituted halogenoacetophenones are decomposed on the aromatic side yielding AcOH and $\text{C}_6\text{H}_4\text{Hal}_2$. 1:3:4:5- $\text{C}_6\text{H}_2\text{MeBr}_3$ is converted by Br at 160—180° when intensely irradiated into 3:4:5-tribromobenzylidene bromide, m.p. 76.5°, hydrolysed by H_2SO_4 at 130—140° to 3:4:5:1- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{CHO}$, m.p. 108°; this is transformed by MgMeI in Et_2O into 3:4:5-tribromophenylmethylcarbinol, b.p. 205—210°/14 mm., oxidised by CrO_3 in AcOH to 3:4:5:1- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COMe}$ (oxime, m.p. 174°), which is transformed by 50% KOH at 150° into resinous matter and 3:4:5- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{CO}_2\text{H}$ (30%). 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{CHO}$ gives 2:4:6-tribromophenylmethylcarbinol, b.p. 195°/17 mm., whence 2:4:6:1- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COMe}$, which is smoothly transformed by 50% KOH at 150° into *s*- $\text{C}_6\text{H}_3\text{Br}_3$ and AcOH. 2:3:4:5-Tetrabromophenylmethylcarbinol, m.p. 142°, gives 2:3:4:5-tetrabromoacetophenone, m.p. 120°, which is very extensively resinsified by KOH. *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ is not greatly changed by 50% KOH at 150° during 24 hr. but is converted by NaOH-KOH at 200—210° into *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ and products of high b.p. Similarly *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ and molten KOH afford *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ (27.5% yield) and complex compounds; *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ gives *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ (39% yield) and complex products but no AcOH. 2:4:1- and 2:5:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{COMe}$ yield respectively 2:4- and 2:5- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$ in 23% and 13% yield. No evidence is obtained of the production of fatty or aromatic acids by the action of molten KOH on 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COMe}$ at 200—210°, 240°, or 260°. CPhMe and KOH-NaOH at 210° give BzOH (yield 31%) but no AcOH. *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ and 10% KOH at 100° give *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. Under similar conditions *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ gives unchanged material and resins but, apparently, very little *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and no AcOH. H. W.

Adrenaline derivatives with nuclear amino-groups. C. MANNICH and G. BERGER (Arch. Pharm., 1939, 277, 117—127).—4:5:2:1-

(OMe) $_2\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{COMe}$ (I) (modified prep.), m.p. 133°, with $\text{SnCl}_2\cdot\text{HCl}$ gives 4:5-dimethoxy-C-methyl-anthranil (II), m.p. 130° (cf. Lawson *et al.*, A., 1924, i, 562), but with $\text{H}_2\cdot\text{PtO}_2$ in COMe_2 gives 2-amino-4:5-dimethoxyacetophenone, m.p. 107° [hydrochloride, m.p. ~202° (decomp.); sulphate, m.p. 200°; *p*-nitrophenylhydrazone, m.p. 192°], the Ac derivative, m.p. 127.5°, of which with Br-AcOH at 80° gives ω -bromo-2-acetamido-4:5-dimethoxyacetophenone, m.p.



163°; with bases this product gives 5:6-dimethoxy-indoxyl. With NaOEt and $C_5H_{11}O \cdot NO$ in EtOH-dioxan (I) gives 2-nitro- ω -oximino-4:5-dimethoxyacetophenone, m.p. 178°. With Br-AcOH (I) gives ω -bromo- (III), m.p. 155°, or $\omega\omega$ -dibromo-2-nitro-4:5-dimethoxyacetophenone, m.p. 150.5°. $(CH_2)_6N_4$ adds to (III) to yield a product, $C_{16}H_{22}O_5N_5Br$, decomp. $\sim 168^\circ$, hydrolysed by HBr-aq. EtOH at 75° to 2-nitro- ω -amino-4:5-dimethoxyacetophenone, amorphous (Ac derivative, m.p. 194.5°; hydrobromide, m.p. 221°). H_2 -PtO₂ then yields ω :2-diamino-4:5-dimethoxyacetophenone (mono-, m.p. 187°, and dihydrobromide, m.p. 243°; Ac₂ derivative, m.p. 211°), converted by 48% HBr into the 4:5-(OH)₂-compound (dihydrobromide, m.p. >280°), which is hydrogenated (PtO₂) to β -hydroxy- β -2-amino-4:5-dihydroxyphenylethylamine, unstable [dihydrobromide, +H₂O, m.p. 132° (decomp.)]. With p -C₆H₄Me·SO₂·NKMe in COMe₂ (III) gives 2-nitro- ω - p -toluenesulphonmethyramido-4:5-dimethoxyacetophenone, m.p. 239°, reduced by SnCl₂-AcOH-HCl to 4:5-dimethoxy- C - p -toluenesulphonmethyramidomethylantranil, m.p. 184°. H_2 -PtO₂ in MeOH-dioxan effects further reduction to 2-amino- ω - p -toluenesulphonmethyramido-4:5-dimethoxyacetophenone, cryst. (Ac derivative, m.p. 176°), which could not be hydrolysed satisfactorily. With NHMe₂ in C₆H₆ (III) gives 2-nitro- ω -dimethylamino-4:5-dimethoxyacetophenone hydrobromide, m.p. 197°, hydrogenated to the 2-NH₂-ketone [hydrobromide, m.p. 192°; Ac derivative, m.p. $\sim 218^\circ$ (decomp.)], which with HBr yields 2-amino- ω -dimethylamino-4:5-dihydroxyacetophenone dihydrobromide, m.p. 249° (decomp.). Attempts to prepare NH₂-alcohols from various products described above failed.

R. S. C.

Condensation of α -methoxystyrene with hydrocarbons. M. A. SPIELMAN and C. W. MORTENSON (J. Amer. Chem. Soc., 1939, 61, 666—667).—OMe·CPh·CH₂ (I) (1 mol.) and PhMe (80 mols.) at 250° give CH₄ and 35% of CPh·[CH₂]₂·Ph (II), but with 1 mol. of PhMe there is mainly the normal rearrangement of (I) to CPhEt and only 8% of (II) is obtained. s -C₆H₃Me₃, PhEt, and p -C₆H₄Me·OMe with (I) at, usually, 250° give similarly β -3:5-dimethylphenylpropionophenone (20.8%), m.p. 54—55° (oxime, m.p. 118°), CPh·CH₂·CHPhMe (23.6%), and p -OMe·C₆H₄·[CH₂]₂·CPh, m.p. 67—68° [semicarbazone, m.p. 135—136° (cf. Bargellini *et al.*, A., 1912, i, 118)], respectively. CH₂Ph₂ gives CPh·CH₂·CHPh₂ (27.3%) and a little (CHPh₂)₂. cycloHexane gives 42.7% of ω -cyclohexylacetophenone, m.p. 17—18°, b.p. 117—118°/1 mm. (oxime, m.p. 104.5—105.5°), also obtained from ZnPhCl and C₆H₁₁·CH₂·COCl in 64% yield, the higher yield being due to the greater no. of available CH₂. CHPh₃, C₆H₆, Ph₂, and p -C₆H₄Me·NO₂ do not react.

R. S. C.

Synthesis of ethyl α -benzoylpropionate. Y. F. CHI, C. C. LEUNG, and W. Y. YÜ (J. Chem. Eng. China, 1938, 5, 42—45).—Prep. of EtCN, EtCO₂Et, CHMeBz·CO₂Et [17% yield from EtOBz (1 mol.), EtCO₂Et (1 mol.), and Na (1 atom) in xylene at 80—90°], b.p. 145—150°/15.6 mm., m.p. 95—98°, and 3-phenyl-4-methylisoxazol-5-one, m.p. 117—118° (lit. 123—124°), is described.

R. S. C.

cis- β -p-Bromobenzoyl- α -methylacrylic acid and its esters. R. E. LUTZ, D. T. MERRITT, jun., and M. COUPER (J. Org. Chem., 1938, 4, 95—100).—The most consistent yields ($\sim 40\%$) of *trans*- β -p-bromobenzoyl- α -methylacrylic acid (I) are obtained from mesaconyl chloride, PhBr, and anhyd. AlCl₃ in PhNO₂ at room temp. It is isomerised by exposure to sunlight in Et₂O but not in EtOH to *cis*- β -p-bromobenzoyl- α -methylacrylic acid (II), m.p. 97°, which is reduced by Zn and conc. AcOH to β -p-bromobenzoyl- α -methylpropionic acid (Me ester, b.p. 147—148°/2 mm.). Conversion of (II) into (I) takes place when a solution of (II) in CHCl₃ containing I is insolated or when (II) is kept in dil. EtOH containing NaOH. (I) is obtained synthetically by the successive action of PCl₅ and PhBr-AlCl₃ in CS₂ on Et H mesaconate. Me *cis*- β -p-bromobenzoyl- α -methylacrylate, b.p. 146°/2 mm., is obtained from (II) and CH₂N₂ or by exposure of the *trans*-ester in EtOH to direct sunlight. Boiling MeOH containing conc. H₂SO₄ transforms (II) into (impure) γ -methoxy- γ -p-bromophenyl- α -methyl- γ -crotonolactone, b.p. 162°/2 mm., slowly hydrolysed by NaOH-dil. EtOH to (I) and unchanged by exposure to sunlight in CHCl₃ containing I.

[With F. B. HILL, jun.] Inversion of *trans*- β -p-bromobenzoyl- β -methylacrylic acid is caused by exposing its solution in MeOH to direct sunlight for 4 hr.; the *cis*-acid (III) is unchanged when insolated for 6 hr. in CHCl₃ containing sufficient I to maintain a colour during the experiment. (III) and CH₂N₂ give a nearly quant. yield of the Me ester identical with that obtained through the Ag salt. H. W.

Cleavage of substituted dibenzoylmethanes on bromination. P. D. BARTLETT and S. G. COHEN (J. Org. Chem., 1939, 4, 88—94).—Bromination of CHBz₃ in hot CHCl₃ gives BzBr and CHBz₂Br. The latter substance is obtained in 60% yield by bromination of CHBz₃ in presence of tetrabromoquinol. In hot AcOH containing C₅H₅N the product of the bromination of CHBz₃ is *tribenzoylmethyl bromide*, m.p. 119—120°. Cleavage requires both Br and HBr. CHPhBz₂, m.p. 144.5—145.6°, is transformed by Br in boiling CHCl₃ into CPhBz₂Br, m.p. 86—87°; evidence of cleavage is not obtained. CH₂Ph·CHBz₂ affords *dibenzoylbzylmethyl bromide*, m.p. 103.5—104°, when brominated in CHCl₃ or in HBr-AcOH. CHPh₂·CHBz₂ is cleaved to CHPh₂Br and CHBz₂Br when brominated in hot CHCl₃ but gives *dibenzoylbzylmethyl bromide*, m.p. 114.5—115.5°, when brominated in AcOH-C₅H₅N. *Dibenzoyltriphenylmethylmethane*, m.p. 148.5—153° (decomp.) (from CPh₃Cl and CHNaBz₂ in C₆H₆), is cleaved to CPh₃Br and CHBz₂Br in both media and has not been brominated normally; with EtOH-NaOEt it gives ω -triphenylmethylacetophenone, m.p. 164—165°. A mechanism for the cleavage is discussed. A boiling EtOH solution of CHPhBz₂ contains at equilibrium 8% of the enolic form.

H. W.

Synthesis from β -naphthaquinol of a tautomeride of 4-benzyl-1:2-naphthaquinone. L. F. FIESER and (Mrs.) M. FIESER (J. Amer. Chem. Soc., 1939, 61, 596—608).—A product obtained from 4-benzyl-1:2-naphthaquinone by boiling alkali or

H_2SO_4 at 0° is shown to be the isomeride, 2-hydroxy-1-keto-4-benzylidene-1 : 4-dihydronaphthalene (I), m.p. $182.5-182.8^\circ$, by independent synthesis. 1 : 2- $\text{C}_{10}\text{H}_6(\text{OH})_2$ (II) and ArCHCl_2 or $\text{ArCHO}-\text{HCl}$ give 2-hydroxy-1-naphthyl aryl-3 : 4-dihydroxy-1-naphthylcarbinyl ethers, which are very sensitive and readily yield compounds analogous to (I). The naphthones add alcohols and Ac_2O at the ends of the conjugated system; this accounts for several abnormal acetates. With CHPhCl_2 alone (II) (modified prep.), m.p. 104° , gives tars, but in C_6H_6 gives 2-hydroxy-1-naphthyl phenyl-3 : 4-dihydroxy-1-naphthylcarbinyl ether (III), darkens at $>100^\circ$, decomp. $>200^\circ$ (solvates with Et_2O , decomp. $106-108^\circ$, or dioxan, m.p. $94-94.5^\circ$), which is vesicant, unstable when kept, and affords the 3 : 4-quinone, decomp. $244-246^\circ$ (uncorr.) (whence an azine acetate, m.p. $284.5-285^\circ$), and, on acetylation, a product, m.p. $229.5-230^\circ$ (III) is also obtained from (II), PhCHO , and dry HCl in C_6H_6 . $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$, (II), and HCl give similarly 2-hydroxy-1-naphthyl p -chlorophenyl-3 : 4-dihydroxy-1-naphthylcarbinyl ether (IV), $+2\text{Et}_2\text{O}$, decomp. $\sim 210^\circ$, which, best by CrO_3 , affords the 3 : 4-quinone, $+ \text{Et}_2\text{O}$, decomp. $\sim 200-210^\circ$, and with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$, $-\text{NaOAc}$, or $-\text{C}_2\text{H}_5\text{N}$ at room temp. gives the triacetate, m.p. $237.5-238^\circ$. $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and Pr^nCHO give 2-hydroxy-1-naphthyl m -nitrophenyl-3 : 4-dihydroxy-1-naphthylcarbinyl, decomp. $>200^\circ$ (triacetate, m.p. $276.5-277^\circ$), and 3 : 4-dihydroxy-1-naphthyl- n -propylcarbinyl ether, cryst. (triacetate, m.p. $166.5-167^\circ$; with H_2SO_4 gives impure products). Crude (III) could not be completely converted into (I), but the solvates or triacetates with conc. H_2SO_4 at 0° give good yields. (I) is also obtained by NaOH in aq. EtOH from phenyl-3 : 4-diacetoxy-1-naphthylcarbinyl acetate [= the "abnormal triacetate," m.p. $139.5-140^\circ$, of its isomeride (Fieser *et al.*, A., 1939, II, 168)]. With $\text{Zn}-\text{Ac}_2\text{O}$, followed by NaOAc , (I) gives 1 : 2 : 4-(OAc) $_2\text{C}_{10}\text{H}_5\cdot\text{CH}_2\text{Ph}$ and a bimol. product, $\text{C}_{12}\text{H}_{13}\text{O}_8$, decomp. $260-265^\circ$, and with amines it yields the same compounds as does 4-benzyl-1 : 2-naphthaquinone [*loc. cit.*; also converted by boiling dil. alkali or conc. H_2SO_4 at 0° into (I)]. Crude (IV) and H_2SO_4 readily give 2-hydroxy-1-keto-4- p -chlorobenzylidene-1 : 4-dihydronaphthalene (V), m.p. $190-190.5^\circ$ (acetate, m.p. $219.5-220^\circ$, prepared by $\text{AcCl}-\text{C}_5\text{H}_5\text{N}$; benzoate, m.p. $229.5-230^\circ$; phenazine derivative, m.p. $243-244^\circ$), reduced to 1 : 2-diacetoxy-4- p -chlorobenzylidene-1 : 4-dihydronaphthalene (VI), m.p. $134.5-135^\circ$ [and a (?) bimol. product, m.p. $>280^\circ$]. With HCl in C_6H_6 , (II) and (V) re-form (IV), a synthesis which proves the structures of the ethers. 2-Hydroxy-1-keto-4- m -nitrobenzylidene-1 : 4-dihydronaphthalene, m.p. $214-214.5^\circ$, is obtained by H_2SO_4 from the corresponding ether. With $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ (V) gives p -chlorophenyl-3 : 4-diacetoxy-1-naphthylcarbinyl acetate, m.p. $138.9-139.2^\circ$ [= the "abnormal triacetate" of the isomeric 3 : 4-quinone] (corresponding tripropionate, m.p. $89-89.5^\circ$), which is hydrolysed to (V) by H_2SO_4 and reduced by $\text{Zn}-\text{Hg}-\text{AcOH}$ to (VI). m -Nitrophenyl-3 : 4-diacetoxy-1-naphthylcarbinyl acetate, m.p. $139.5-140^\circ$ (corresponding tripropionate, m.p. $142.5-143^\circ$), is similarly prepared. 4-Di(carbethoxy)methyl-1 : 2-naphthaquinone or its tautomeric naphthone with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ gives first the acetate and then 1 : 2-

diacetoxy-4-acetoxydicarbethoxymethylnaphthalene, m.p. $140.5-141^\circ$, hydrolysed by acid to the original quinone and also obtained from 1 : 2 : 4-(OAc) $_2\text{C}_{10}\text{H}_5\cdot\text{CH}(\text{CO}_2\text{Et})_2$ by $\text{Pb}(\text{OAc})_4$ in AcOH at 100° ; this latter synthesis proves the structure of the abnormal triacetates. With MeOH or EtOH and a drop of H_2SO_4 the naphthones give 30-80% yields of 4- α -methoxy-, m.p. $133.5-134^\circ$, and 4- α -ethoxybenzyl-1 : 2-naphthaquinone, m.p. $154.5-155^\circ$, 4- p -chloro- α -methoxy- (VII), m.p. $172.5-173^\circ$ (phenazine derivative, m.p. $202-202.5^\circ$), and 4- p -chloro- α -ethoxy- (VIII), m.p. $144-144.5^\circ$ (phenazine derivative, m.p. $203-203.5^\circ$), -benzyl-1 : 2-naphthaquinone. Reductive acetylation of (VII) gives 1 : 2-diacetoxy-4- p -chloro- α -methoxybenzylidene-1 : 4-dihydronaphthalene, m.p. $134-134.5^\circ$. Hydrolysis of (VIII) by cold, conc. H_2SO_4 gives (V). 3-Hydroxy-2-benzyl-1 : 4-naphthaquinone (IX) by reductive acetylation gives the quinol triacetate, m.p. $179-180^\circ$ (uncorr.), but with $\text{Ac}_2\text{O}-\text{NaOAc}$ gives first a substance, m.p. $120-121^\circ$ (uncorr.), and then phenyl-1 : 3 : 4-triacetoxy-2-naphthylcarbinyl acetate, m.p. $193.5-194^\circ$ (uncorr.), which in $\text{EtOH}-\text{NaOH}$ in N_2 is hydrolysed to (IX). Hydrolapachol, however, gives only the monoacetate, and the Me ether, m.p. $83-83.5^\circ$, of (IX) is unchanged. Acetylation of lapachol is discussed as an example of this 4-alkyl-1 : 2-naphthaquinone \longleftrightarrow 2-hydroxy-1-keto-4-alkylidene-1 : 4-dihydronaphthalene isomerism, which seems to be fairly general. M.p. are corr. R. S. C.

Reduction of 2 : 2-dialkylated 1 : 3-diketones; electrolytic reduction of dimethylmethone [2 : 2 : 5 : 5-tetramethylcyclohexane-1 : 3-dione]. N. J. TOIVONEN and V. P. HIRSKJÄRVI (Suomen Kem., 1939, 12, B, 2-3).—Electrolytic reduction (Pt anode, Hg cathode) of dimethylmethone in aq. EtOH and CO_2 gives 2 : 2 : 5 : 5-tetramethylcyclohexan-1-ol-3-one, m.p. $51-51.5^\circ$ [semicarbazone, m.p. $191-196^\circ$ (decomp.)], reduced (electrolytically or $\text{Na}-\text{EtOH}$) to the -1 : 3-diol, m.p. $205-206^\circ$. A. T. P.

Unsaturated steroids. V. Rearrangements and structure of steroid peroxides. W. BERGMANN, F. HIRSCHMANN, and E. L. SKAU (J. Org. Chem., 1939, 4, 29-39; cf. A., 1938, II, 227; 1939, II, 14).—Exposure of 2 : 5-peroxido- Δ^3 -cholestene (I) in abs. EtOH to sunlight leads to ketone A, m.p. 172° , $[\alpha]_D^{25} +141^\circ$ in CHCl_3 (monoxime, m.p. $225-229^\circ$), which does not appear to contain a double linking (titration with BzO_2H) and shows only general absorption below $250\text{ m}\mu$. When treated with Ac_2O or distilled under 1 mm . A is isomerised to ketone B, $\text{C}_{27}\text{H}_{44}\text{O}_2$, m.p. 173° , $[\alpha]_D^{25} +36.0^\circ$ in Et_2O [semicarbazone, m.p. 234° (decomp.)], which resembles A in absorption spectrum and behaviour towards BzO_2H . $\text{KOH}-\text{MeOH}$ transforms A or B into ketone C, $\text{C}_{28}\text{H}_{48}\text{O}_3$, m.p. $153.5-154^\circ$, $[\alpha]_D^{25} +35.4^\circ$ in CHCl_3 [semicarbazone, m.p. $251-254^\circ$ (decomp.)], also obtained similarly from (I). It contains 1 OMe and is therefore probably formed by some type of addition of MeOH to the mol. It differs from A and B in that it does not absorb ultra-violet light in the region measured. It does not react with BzO_2H or Ac_2O . When distilled/1 mm. C loses 1 MeOH and forms B. Catalytic hydrogenation (PtO_2) of A, B, or C causes absorption of 1 H_2 with formation of OH-compounds.

The structure of steroid peroxides and their rearrangement products is discussed. All m.p. are corr. H. W.

Photo-chemistry of cholestenone. H. H. INHOFFEN and H. MINLON (Naturwiss., 1939, 27, 167).—The substance, $C_{22}H_{32}O_2$, obtained by Bergmann *et al.* (A., 1939, II, 119) by ultra-violet irradiation of Δ^4 -cholestenone (I) is most probably $C_{22}H_{32}O_2$ (or, less likely, $C_{22}H_{30}O_2$), m.p. $\sim 370^\circ$. When rapidly distilled at 20 mm., it gives (I), and is apparently 4-4'-cholestanonyl- Δ^5 -cholestenone [or, less probably, di-(Δ^5 -4-cholestenonyl)], the two nuclei being united probably through $C_{(4)}$ and $C_{(4')}$. W. O. K.

Sterols. LII. Reduction products of progesterone and the pregnanediones. R. E. MARKER and E. J. LAWSON (J. Amer. Chem. Soc., 1939, 61, 588—590; cf. A., 1937, 505).— H_2 - PtO_2 at 3 atm. converts progesterone in EtOH into pregnane-3(α):20(β)- and allopregnane-3(β):20(β)-diols, separable by digitonin. Hydrogenation of allopregnane-(I) [to the 3(β):20(β)-diol] or pregnane-dione (II) or the corresponding 3(α)-ol-20-ones in AcOH gives always diols having the β -configuration at $C_{(20)}$; some 3(α):20(β)-diol [but mainly the 3(β):20(β)-diol] is formed from (II). A little 3(α):20(β)-diol is also formed [with (mainly) the 3(β):20(β)-diol] from (II) in presence of HBr, but (I) gives similarly 60% of the 3(α):20(β)- and 17% of the 3(β):20(β)-diol. Partial reduction of (I) in AcOH-HBr to allopregnane-3(α):20(β)-diol, (III) (below), and (?) *epiallopregnane*-3(α)-ol-20-one (cf. Fleischer *et al.*, A., 1938, II, 103) is best effected at room temp./2.6 atm.; in AcOH alone allopregnane-3(β)-ol-20-one (III), m.p. 193° (acetate, m.p. 143°), is obtained. In EtOH (no acid) (II) gives mainly pregnane-3(α)-ol-20-one. R. S. C.

Sterols. LI. Δ^4 -Pregnen-3-one. R. E. MARKER and E. J. LAWSON (J. Amer. Chem. Soc., 1939, 61, 586—587; cf. A., 1938, II, 497).—Pregnan-3(α)-ol-20-onesemicarbazone, m.p. 246° , and NaOEt-EtOH at 180° give 85% of pregnane-3(α)-ol with a little of the β -epimeride. This mixture with CrO_3 gives pregnane-3-one, the 4-Br-derivative, m.p. 137° , of which with C_5H_5N gives a mixture, separated by adsorption on Al_2O_3 , of Δ^4 -pregnen-3-one, m.p. 90° (semicarbazone, m.p. 216° ; 2:4-dinitrophenylhydrazone, m.p. 198°), and the pyridinium bromide, $C_{26}H_{38}ONBr$, m.p. 235° . R. S. C.

Steroids and sex hormones. L. Rearrangement of tert. vinyl alcohols of the androstene series. L. RUZICKA and P. MÜLLER. **LI. Neopregnenolone from Δ^5 -3:17-dihydroxypregnen-20-one.** L. RUZICKA and H. F. MELDAHL (Helv. Chim. Acta, 1939, 22, 416—420, 421—424; cf. A., 1938, II, 413; 1939, II, 76, 157).—L. 17-Vinylandrosten-3:17-diol 3-acetate (cf. A., 1938, II, 186) and PBr_3 - $CHCl_3$ (+ a little C_5H_5N) at -20° to room temp. (24 hr.) give Δ^5 :17-21-bromo-3-trans-acetoxypregnadiene, m.p. 144° (one experiment gave a stereoisomeride, m.p. 208°), converted by KOAc in AcOH, or better in $COMe_2$, at room temp. (3 days) into Δ^5 :17-3-trans:21-diacetoxypregnadiene, m.p. 135 — 136° , which with KOH-MeOH gives Δ^5 :17-pregnadiene-3:21-diol, m.p. 198 — 199° , $[\alpha]_D^{25}$ $-59.5 \pm 1.5^\circ$ in

EtOH. The last two compounds are identical with those of Miescher and Scholz (A., 1939, II, 157). 17-Vinyltestosterone (A., 1938, II, 284) and PBr_3 - $CHCl_3$ (+ C_5H_5N) at room temp. give Δ^4 :17-21-bromopregnadiene-3-one, m.p. 126 — 127° , converted (KOAc- $COMe_2$) into the 21-acetate, m.p. 107° , of Δ^4 :17-21-hydroxypregnadiene-3-one, m.p. 138 — 139° , $[\alpha]_D^{25}$ $+116.5^\circ$ in EtOH (cf. Miescher).

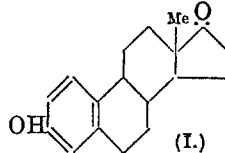
LI. Δ^5 -17-Hydroxy-3-trans-acetoxypregnen-20-one (A., 1939, II, 76) and PBr_3 - C_6H_6 give the corresponding 17-bromide, m.p. 148 — 150° , which with Zn -AcOH affords neopregnenolone acetate, m.p. 179 — 180° , $[\alpha]_D^{25}$ -117° in EtOH (Miescher and Kägi, A., 1939, II, 166), hydrolysed (KOH-MeOH) to neopregnenolone, m.p. 220 — 222° , $[\alpha]_D^{25}$ -125° in dioxan (oxime, m.p. 229 — 231°). Physiological tests are recorded. A. T. P.

Sex hormone series. IV. New method of preparing pregnenolone. H. H. INHOFFEN and H. KÖSTER (Ber., 1939, 72, [B], 595—596; cf. A., 1938, II, 284).—Addition of androstenedione 3-enol Et ether in C_6H_6 -Et₂O to CH_3CK in liquid NH_3 and hydrolysis of the product by 10% HCl gives pregnenolone-17-ol-3-one, m.p. 265 — 267° . H. W.

Esters of œstrone with fatty acids.—See B., 1939, 437.

Syntheses in the hydroaromatic series. V. Synthesis of an isomeride of œstrone. E. DANE and J. SCHMITT (Annalen, 1939, 537, 246—249).—

The OMe-diketone, $C_{19}H_{20}O_3$ (A., 1939, II, 27), is hydrogenated (Pd-C) to the ketol, $C_{19}H_{24}O_3$, m.p. 167° , converted by HBr-AcOH followed by NaOH into the unsaturated OH-ketone, $C_{18}H_{20}O_2$, m.p. 244 — 245° (decomp.). This is hydrogenated to the isomeride (I), m.p. 210° , of œstrone. H. W.



Synthesis of steroid glycuronides. E. SCHAPIRO (Biochem. J., 1939, 33, 385—388).—Additions to work already reported (A., 1939, II, 119). Me triacetatebromoglycuronate in C_6H_6 + Ag_2CO_3 gives with dehydroandrosterone, testosterone, α -œstradiol 3-benzoate, œstrone, and cholesterol the corresponding acetylated glycuronides, (I), m.p. 193 — 196° , $[\alpha]_D^{25}$ -19.7° in $CHCl_3$, -16.2° in C_6H_6 , (II), m.p. 186 — 189° , $[\alpha]_D^{25}$ $+28.3^\circ$ in $CHCl_3$, (III), m.p. 188 — 191.5° , $[\alpha]_D^{25}$ $+9.2^\circ$ in $CHCl_3$, (IV), m.p. 225.5 — 228° , $[\alpha]_D^{25}$ $+57.1^\circ$ in $CHCl_3$, and m.p. 162 — 164.5° (softening $\sim 152^\circ$), respectively. (I) and (II) applied by smearing on capon's combs are inactive; (III) and (IV) on subcutaneous injection into castrated mice produce œstrus. Hydrolysis of (I) and (III) gives dehydroandrosterone, m.p. 262 — 264° (decomp.) (inactive), and α -œstradiol-17-glycuronic acid, m.p. 191 — 194.5° (œstrus-producing), respectively. S. H. H.

Fate of Δ^3 -12-ketocholenic acid in the rabbit. Synthesis of dehydronorcholadiene. T. MORI (Z. physiol. Chem., 1939, 258, 143—146; cf. Kyogoku, A., 1937, II, 150).—The urine of rabbits to which Δ^3 -12-ketocholenic acid (I) (35 g.) has been intravenously administered yields deoxycholic acid (3.1

g.; 120 c.c. of bile also yield 4.6 g.). When 3-hydroxy-12-ketocholanic acid is gradually heated to 250—280°/high vac., maintained at this temp. for 50 min., then heated to ~300°, and finally at 350—370°, (I) and *dehydronorcholadiene*, $C_{23}H_{34}$, m.p. 107° [reduced (H_2 , PtO_2 , AcOH) to *dehydronorcholane*], distil.

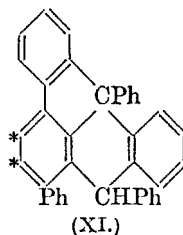
W. McC.

Quinhydrones. IV. L. BRÜLL and M. MINCHILLI (Gazzetta, 1939, 69, 41—44).—An equimol. mixture of *p*-NPh· C_6H_4 ·NPh (I) and *p*- C_6H_4 (NHPH) $_2$ (II) in EtOH with 10% aq. HI gives a compound, $C_{36}H_{32}N_4I_2$, m.p. 160°, regarded as $[RM]I_2$, where $R = \cdot NPh \cdot C_6H_4 \cdot NHPH \cdot$, and $M = (II)$. (I) + (II) with aq. picric acid (2 equivs.) gives the merquinoid *monopicrate*, $C_{42}H_{33}O_7N_7$, m.p. 147°, of 1 mol. each of (I) and (II); the *perchlorate*, $C_{36}H_{33}O_8N_4Cl_2 \cdot 12H_2O$, m.p. 140°, is obtained similarly in $COMe_2$.

E. W. W.

Phenylated phthalic acids and anthracene derivatives. C. WEIZMANN, E. BERGMANN, and L. HASKELBERG (J.C.S., 1939, 391—397).—3 : 6-Diphenyltetrahydrophthalic anhydride and S at 260—270° give quantitatively 3 : 6-diphenylphthalic anhydride (I), m.p. 224°, which is hydrolysed to the acid, m.p. 162° (decomp.) (*Me* $_2$ ester, m.p. 188°), by hot aq. Na_2CO_3 . With the appropriate Grignard reagent, (I) gives 2-benzoyl-, m.p. 167°, 2-p-bromobenzoyl-, m.p. 200°, 2- α -naphthoyl-, m.p. 188°, 2-p-anisoyl-, +2 H_2O , double m.p. 125° and 175° (*Me* ester, m.p. 185°), and 2-6'-methoxy- β -naphthoyl-3 : 6-diphenylbenzoic acid, m.p. 220° after sintering (*Me* ester, m.p. 220°). Ring-closure of the keto-acids is difficult, probably owing to steric hindrance, and H_2SO_4 causes sulphonation. 3 : 6-Diphenylphthalimide, m.p. 245°, is obtained from (I) only by $CO(NH_2)_2$ at 200° and does not yield the NH_2 -acid, but its *N*-OH-derivative, m.p. 238° [readily prepared from (I) and NH_2OH in EtOH at room temp.], with aq. NaOH at 100° gives 3 : 6-diphenylanthranilic acid, m.p. 200° (decomp.) (*Me* ester, m.p. 119—120°; *Ac* derivative, m.p. 215°), which, however, does not react with $CH_2Cl \cdot CO_2H$, $CH_2Br \cdot CO_2H$, or $CH_2O \cdot KCN$. With $AlCl_3$ in hot C_6H_6 , (I) yields 2-phenylfluorenone-1-carboxylic acid (II), m.p. 199—201° (phenylhydrazone, m.p. 177°), the *Me* ester, m.p. 142°, of which with $MgPhBr$ gives 1-benzoyl-2-phenylfluorenone (III), m.p. 236°; $LiPh$ in Et_2O , however, gives 2 : 9-diphenyl-1- α -hydroxybenzhydryl-9-fluorenone, m.p. 123° (decomp.), and some (III). With Cu-bronze in boiling quinoline, (II) gives 2-phenylfluorenone, m.p. 140—141° (phenylhydrazone, m.p. 168°). With hot $SOCl_2 \cdot CCl_4$, (II) is further cyclised to 1'-ketoindeno-2' : 3'-1 : 2-fluorene-9-one, m.p. 298° [di(phenylhydrazone), m.p. 215° (decomp.)]. 3-Phenylphthalic anhydride, m.p. 143°, is obtained from its H_4 -derivative by S at 280° and with $MgPhBr$ in hot C_6H_6 gives (?) 6-benzoyl-2-, m.p. 163°, and some (?) 2-benzoyl-3-phenylbenzoic acid, m.p. 172°. ($CH \cdot CO_2O$) does not condense with (*p*-OMe· C_6H_4 ·CH·CH) $_2$ or (CHPh·CPh) $_2$. 1-Phenylanthraquinone, obtained from α -naphthaquinone (IV) and CHPh·CH·CH·CH $_2$ (V) at 180°, is converted by $MgPhBr$ (10 mols.) into 9 : 10-dihydroxy-1 : 9 : 10-triphenyl-9 : 10-dihydroanthracene, m.p. 238°, and by Zn dust in aq. NH_3 -NaOH into 1-phenylanthracene, m.p. 123°. *p*-O· C_6H_4 ·O (VI) in boiling xylene with (V) gives (?)

1 : 5-diphenyl-1 : 4 : 5 : 8 : 11 : 12 : 13 : 14-octahydroanthraquinone (VII), m.p. 230°, and (?) 5-phenyl-5 : 8 : 9 : 10-tetrahydro- α -naphthaquinone, m.p. 170°. Air converts (VII) in boiling 15% KOH-EtOH into 1 : 5-diphenylanthraquinone, m.p. 355°. Heating (VI) with (CHPh·CH) $_2$ (VIII) yields 1 : 4 : 5 : 8-tetraphenylanthraquinone, m.p. 355°, converted by $LiPh$ into 9 : 10-dihydroxy-1 : 4 : 5 : 8 : 9 : 10-hexaphenyl-9 : 10-dihydroanthracene, m.p. >370°. At 160° (IV) and (VIII) give 1 : 4-diphenylanthraquinone (IX), m.p. 212° [$(NO_2)_2$, m.p. ~208°, Br_2 , m.p. 295°, and Br_4 -derivative, m.p. >300°; Na_2 disulphonate, +3 H_2O], converted by Zn dust in aq. NH_3 -NaOH into 1 : 4-diphenyl- (X), m.p. 170° (picrate, m.p. 173°), and 9-hydroxy-1 : 4-diphenyl-9 : 10-dihydroanthracene, m.p. 155° [with HCl-EtOH gives (X)]. With $MgPhBr$ in hot C_6H_6 , (IX) gives 9 : 10-dihydroxy-1 : 4 : 9 : 10-tetraphenyl-9 : 10-dihydroanthracene, m.p. 240°, converted by hot HCO_2H or $AcCl$ into the hydrocarbon (XI), m.p. 322°, also obtained with 1 : 4 : 9 : 10-tetraphenylanthracene (XII), m.p. 205°, by $KI-Na_2S_2O_4$ in AcOH at 80°. Hot HCO_2H converts (XII) into (XI). It follows by analogy that ψ -rubrene is probably the

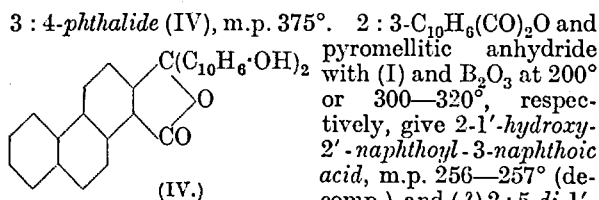


**benzo-derivative of (XI) (cf. Dufraisse, A., 1936, 1499).

R. S. C.

Sulphonation of 1 : 2-benzanthraquinone and mesobenzanthrone. J. S. JOFFE (Prom. Org. Chim., 1939, 6, 95—97).—The products of sulphonation are 1 : 2-benzanthraquinone-3'-(? quinone salt, m.p. 202—205°), 4'-, and -5'-sulphonic acid, and benzanthrone-1-, -2-, and -3-sulphonic acid (? quinone salt, m.p. 240—242°) (cf. A., 1936, 1381; 1939, II, 74). α - $C_{10}H_7 \cdot COPh$ yields 1 : 5- $C_{10}H_6BzSO_3H$. R. T.

Boric acid synthesis of peri-hydroxyanthraquinones. C. WEIZMANN, L. HASKELBERG, and (in part) T. BERLIN (J.C.S., 1939, 398—401).—In presence of B_2O_3 α - $C_{10}H_7 \cdot OH$ derivatives and phthalic anhydrides give CO_2 -acid, the aroyl entering *o*- to the OH, whereas with 1- $C_{10}H_7 \cdot OMe$ derivatives the 4-position is attacked. In the former case reaction probably occurs by formation of a H phthalate, followed by a Fries rearrangement. With 1 : 4- $C_{10}H_6(OH)_2$ derivatives condensation leads directly to derivatives of dihydroxynaphthacenequinones. α - $C_{10}H_7 \cdot OH$ (I), 3 : 6 : 1 : 2- $C_6H_4Ph_2(CO)_2O$ (II), and B_2O_3 at 200—220° give 2-1'-hydroxy-2'-naphthoyl-3 : 6-diphenylbenzoic acid, m.p. 214° [*Ac* derivative, m.p. 243°; *Me* ether *Me* ester (prep. by CH_2N_2), m.p. 168°], which does not yield a quinone; hot H_2SO_4 causes sulphonation as well as ring-closure. 1 : 5-OH· $C_{10}H_6 \cdot OMe$ with (II) and B_2O_3 gives similarly only 2-1'-hydroxy-5'-methoxy-2'-naphthoyl-3 : 6-diphenylbenzoic acid, m.p. 210° (sinters at 205°), but with *o*- $C_6H_4(CO)_2O$ (III) and $AlCl_3$ in $PhNO_2$, first at room temp. and then at 50°, gives about equal amounts of 5-methoxy-2- and -8-*o*-carboxybenzoyl- α -naphthol, m.p. 221° and 247°, respectively or vice versa. Phenanthrene-1 : 2-dicarboxylic anhydride (prep. from the H_2 -derivative by Se at 300—325°), m.p. 311—312°, with (I) and B_2O_3 at 260° gives α -di-(4''-hydroxy-1''-naphthyl)naphtha-2' : 1'-



R. S. C.

Chlorination of menthane. A. GANDINI (Gazzetta, 1938, 68, 779—792; cf. A., 1936, 1257).—Menthane (I) with Cl₂ in CCl₄ (sunlight) gives (1 Cl₂) 4-chloromenthane (II) and (2 Cl₂) 2 : 4-dichloromenthane (III), b.p. 140—142°/30 mm. With NH₃Ph, (II) forms *dl*-Δ³-menthene, and with aq. KOH, menthan-4-ol, also obtained by reducing Δ¹-menthen-4-ol. With quinoline, (III) gives a mixture of α- and γ-terpinene; with MeOH-NaOMe, (mixed ?) chloromenthene(s), hydrogenated to 2-chloromenthane; and with AgOAc-Ac₂O, *dl*-carvomenthol. Chlorination products of (I) also include tri-, tetra-, and penta-chloromenthanes.

E. W. W.

Phellandrene nitrosites. I. α- and β-Nitrosites of *l*-α-phellandrene. P. A. BERRY, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1939, 466—470).—On crystallisation from COMe₂, MeOH, and other solvents the β-nitrosite is readily converted in part into the α-isomeride, but the yields are never large, as other mutarotation products are formed. Specimens of the β-compound having [α]_D²⁰ -260·1° in CHCl₃ and m.p. 96° have been obtained but this may not be the max val. obtainable. Mutarotation curves indicate that the labile β-nitrosite is converted into the stable cryst. α-form.

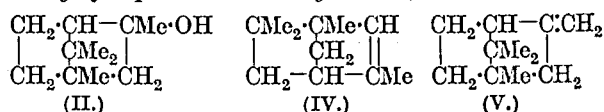
F. R. S.

Action of acetic acid on α-pinene in presence of boron triacetate. M. IMOTO (J. Soc. Chem. Ind. Japan, 1938, 41, 443—444B).—The reaction has been carried out under varying conditions and the products investigated. Borneol, isoborneol, camphene, dipentene, fenchyl alcohol, and some polymerised substances are produced.

A. LI.

epiCamphor series. New fenchene homologues and 4-methylisofenchone. G. A. NYMAN and A. M. KUVAJA (Annalen, 1939, 538, 68—84).—*dl*-epiCamphor (I) and MgMeI give much unchanged ketone and 3-methylepiborneol (II), b.p. 88—90°/15

mm., m.p. 59—60°. This is dehydrated by KHSO₄ to a mixture (III), which is separated into 4-methyl-γ-fenchene (IV), b.p. 159—163°, and 4-methyl-α-fenchene (V), b.p. 167—170°. Ozonisation of (IV) gives the non-cryst. (?) 4-acetyl-1 : 2 : 2-trimethylcyclopentane-1-carboxylic acid, which could not



be caused to react with NH₂·CO·NH·NH₂ but freely affords CHBr₃ when treated with NaOBr, giving a non-cryst. dicarboxylic acid. Ozonisation of (V) yields (I). Hydration of (III) by 50% H₂SO₄ in AcOH at 60—65° gives sec.-4-methylisofenchyl acetate, b.p. 107—109°/15 mm. (yield 82%), hydrolysed by KOH-EtOH to sec.-4-methylisofenchol (VI), b.p. 98—100°/16 mm., m.p. 50—54° (*H* phthalate, m.p. 146—147°; phenylurethane, m.p. 75—76°). Gradual addition of (VI) to a mixture of HNO₃ (*d* 1·42 and 1·52) at room temp. yields 4-methylisofenchone, b.p. 212—215° (semicarbazone, m.p. 195°). Oxidation of (VI) suspended in dil. KOH by KMnO₄ at 60° affords 3-methylisofenchocamphoric acid, m.p. 197—198°, which readily yields an anhydride, m.p. 129—130°, but is not substituted when treated successively with PCl₅ and Br. Dehydration of (VI) gives mixed hydrocarbons (VII), b.p. 161—167°, degraded by O₃ to (?) 4-methyl-β-fenchocamphorone, m.p. 155—156° (semicarbazone, m.p. 221—223°). This is oxidised by KMnO₄ to a 3-methylapofenchocamphoric acid, m.p. 189—191°, and (?) 4-methyl-β-fenchenylic acid, C₁₁H₁₈O₂, m.p. 115—117°. (VII) must therefore contain 4-methyl-β-fenchene.

H. W.

Diterpenes. XXXVII. Synthesis of geranylgeraniol. L. RUZICKA and G. FIRMENICH (Helv. Chim. Acta, 1939, 22, 392—396; cf. A., 1938, II, 287).—Nerolidol and PBr₃-C₃H₅N at -15° (method : cf. Juwala, A., 1930, 1401; Karrer *et al.*, A., 1931, 333) gives farnesyl bromide, converted by CH₂Ac·CO₂Et-Na-EtOH into (Girard reagent T) farnesylacetone, b.p. 147—148°/0·5 mm. The latter and C₂H₅-KOBut-Et₂O at 0° to room temp. give geranyldihydrolinalool, b.p. 129—131°/0·05 mm., partly hydrogenated (1·05 mol. H₂; CaCO₃-Pd) to geranyllinalool, b.p. 134°/0·1 mm. The latter (as above) affords geranylgeranyl bromide, CH₂R·CMe·CH·CH₂Br (R = farnesyl), which in COMe₂-KOAc at room temp., then KOH-MeOH, yields geranylgeraniol, b.p. 152—153°/0·07 mm. (distilled in N₂) (purified through the phthalate). Similarly, nerolidol gives, through farnesyl bromide and acetate, farnesol.

A. T. P.

Triterpenes. XLIV. Conversion of oleanol-lactonedicarboxylic acid- into ketodihydro-oleanolic acid-derivatives. L. RUZICKA, F. C. VAN DER SLUYS-VEER, and S. L. COHEN (Helv. Chim. Acta, 1939, 22, 350—360; cf. A., 1936, 477; 1938, II, 29).—Me *H* isooleanol-lactonedicarboxylate and CrO₃-AcOH at room temp. give Me *H* isooleanonelactone-dicarboxylate, m.p. 258—259° (all m.p. are corr.)

(oxime, m.p. 273—274°). Pyrolysis at atm. pressure in CO₂ gives (Girard reagent T in EtOH-AcOH) a ketone, C₁₄H₂₂O, b.p. 90—100°/0.04 mm. (its formation by fission is discussed) (semicarbazone, C₁₅H₂₅ON₃, m.p. 189—190°), and a hydrocarbon, b.p. 120—130°/14 mm., dehydrogenated by Se at 340—350° to give some 2 : 7-C₁₀H₆Me₂. Me acetylketo-dihydro-oleanolate and CrO₃-AcOH at 80° afford acetyldiketo-oleanolactone (I), C₃₂H₄₆O₆, m.p. 270—272° (absorption spectra) (hydrolysed by KOH-EtOH to the diketo-oleanol-lactone, C₃₀H₄₄O₅, m.p. 330—333°), and (?) Me H₂ acetylhydroxyoleanoltricarboxylate, m.p. 290—292°, C₃₃H₅₂O₉, or the lactone, C₃₃H₅₀O₈ (structural formula suggested). Me acetylketo-oleanolate and CrO₃-AcOH-H₂SO₄ at 20—30° afford (I). The formula of oleanolic acid and its derivatives is discussed (cf. *loc. cit.*, and Picard *et al.*, A., 1939, II, 121).

A. T. P.

Lignin and related compounds. XXXVII. Structure of lignin and the nature of plant synthesis. H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 725—731; cf. A., 1939, II, 172).—Possible biosyntheses of lignins, tannins, and pigments from MeCHO or its dismutation products are discussed. Inositol and CH₂<CH(OH)·C(OH)₂>CH₂ are important intermediates.

R. S. C.

Action of ethylenediamine-copper oxide solution on wood and straw. R. S. HILPERT and J. PRÜTZENREUTER (Ber., 1939, 72, [B], 607—610).—About 60% of white beech is dissolved by (CH₂·NH₂)₂-CuO and, apart from an increase in the % OMe, the composition of the residue does not differ appreciably from that of the original wood. Red beech behaves similarly but is less extensively dissolved. The substance obtained by addition of acid to the alkaline solution contains only 0—3% N and has the composition C₆H₁₀O₅. Pine and fir are less attacked than beech. The high C content of the residue from pine is very characteristic; otherwise it yields with acids the customary amount of lignin with the usual OMe content. A concn. of the lignin in the residue has not occurred so that the high C content must have another cause. The ppt. obtained by acidifying the alkaline solution has the composition of cellulose; it yields only 8% of lignin with 11.2% OMe. Fir is little attacked and is distinguished from the other woods since the product pptd. from the solution contains less H₂O than does cellulose. Straw is dissolved by (CH₂·NH₂)₂-Cu(OH)₂ leaving 14% of residue which, according to elementary analysis, appears to have acquired H₂O whilst the % OMe remains const. When heated with acids it gives less lignin than does straw and the % OMe of the product is 10.5% compared with 14%. Acids ppt. > half of the straw substance from the solution; its elementary composition corresponds with that of straw but the % OMe is less; it contains 0.3% N. The results afford further evidence in favour of the view that the lignins are reaction products and not components. H. W.

Action of alkaline hypobromite on aloin. E. J. SCHORN (Pharm. J., 1939, 142, 300).—Barbaloin and NaOBr-NaOH yield CBr₄ and H₂C₂O₄. J. D. R.

Constitution of fustin. T. OYAMADA (Annalen, 1939, 538, 44—67).—An account of work already abstracted (A., 1935, 757). H. W.

Deaminocozymase, C₂₁H₂₆O₁₅N₆P₂, and its dihydro-derivative.—See A., 1939, III, 424.

Constituent of the root of *Ononis spinosa*, L. F. NEUWALD (Arch. Pharm., 1939, 277, 130—132).—Steam-distillation of this root gives ~0.2% of a volatile oil, containing ~ half its wt. of spinosin, C₂₅H₄₂O, m.p. 149°, for which colour reactions are described. R. S. C.

Fixation of aromatic double bonds in the chromones. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 1—6).—7-Allyloxyflavone, m.p. 95—96° (from 7-hydroxyflavone, C₉H₅Br, and K₂CO₃ in COMe₂), when heated at 210—215° for 2½ hr. yields 7-hydroxy-8-allylflavone (+ H₂O) (I), m.p. 245—246°, also obtained by heating 3-allylresacetophenone with NaOBz and Bz₂O, and hydrolysing (EtOH-KOH) the product. This is converted into 7-allyloxy-8-allyl-, m.p. 145—146°, which on heating yields 7-hydroxy-6 : 8-diallyl-flavone, m.p. 196—198°. By similar reactions 3-methoxy-7-allyloxy-2-methylchromone, m.p. 94—95°, gives 3-methoxy-7-hydroxy-8-allyl- (+H₂O), m.p. 183—184°, -7-allyloxy-8-allyl-, m.p. 66—68°, and -7-hydroxy-6 : 8-diallyl-2-methylchromone (+0.5H₂O), m.p. 120—121°. (I), 7-hydroxy-8-methyl- (+H₂O), m.p. 255—257° [from 1 : 3 : 4 : 2-C₆H₂Me(OH)₂·COMe, NaOBz, and Bz₂O], and 7-hydroxy-3-methoxy-8-methylflavone all give dyes with diazotised *p*-NO₂·C₆H₄·NH₂. A. Li.

7-Hydroxychromone-8-aldehydes and their conversion into chromono-7 : 8-α-pyrones. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 7—9).—7-Hydroxychromones do not condense (H₂SO₄) with malic acid. 7-Hydroxy-, m.p. 223—224°, and 7-hydroxy-3-methoxy-flavone-8-aldehyde, m.p. 222—223° (phenylhydrazone, m.p. 149—151°) [reduced (Pd-C) to the -8-methylflavone], and 7-hydroxy-3-methoxy-2-methylchromone-8-aldehyde, m.p. 180—181° (phenylhydrazone, m.p. 220—222°), are prepared from the 7-hydroxychromones by heating with (CH₂)₆N₄ in AcOH, and hydrolysing the product with conc. HCl. These when heated with NaOAc and Ac₂O yield the corresponding chromono-7 : 8-α-pyrones, m.p. 250°, 254—255°, and 282—284° respectively. A. Li.

Reactivity of the double bond in coumarins and related unsaturated carbonyl compounds. VII. Action of mercuric acetate on hydroxy- and 4-methyl-coumarins. P. S. RAO, V. D. N. SASTRI, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 22—28; cf. A., 1930, 487; 1934, 1107; 1936, 1516).—With Hg(OAc)₂ in MeOH-AcOH, 7-hydroxycoumarin yields 7-hydroxy-4-methoxy-3 : 6 : 8-triacetoxymercurimilotic anhydride, decomp. 232°, converted by H₂S into 4-hydroxycoumaric acid, and by H₂SO₄-HNO₃ into 3 : 6 : 8-trinitro-7-hydroxycoumarin; 7-hydroxy-4-methylcoumarin (I) yields 7-hydroxy-8-acetoxymercuri-4-methylcoumarin, decomp. 246°, which reverts to (I) with H₂S, and when nitrated yields the 8-NO₂-compound; and 4 : 7-dimethylcoumarin (II) yields (slowly) 4-methoxy-

3 : 6-diacetoxymercuri-4 : 7-dimethylmelilotic anhydride, decomp. 242° , which with H_2S gives β : 4-dimethylcoumaric acid [converted into (II) when boiled with EtOH], and with Br in AcOH gives 3 : 6-dibromo-4 : 7-dimethylcoumarin, hydrolysed (EtOH-KOH) to 4-bromo-2 : 5-dimethylcoumarilic acid. A. Li.

Egonol. VII. Synthesis of dihydroconiferyl alcohol and styraxinaldehyde, the two products of the degradation of egonol. Reaction mechanism of the flavylium salt synthesis. S. KAWAI and N. SUGIYAMA [with, in part, T. NAKAMURA and F. YOSHIMURA] (Ber., 1939, 72, [B], 367—380; cf. A., 1939, II, 80, 125).—2 : 4 : 1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ is converted by allyl bromide and anhyd. K_2CO_3 in dry COMe_2 into 4-methyl-6-allylguaiacol, b.p. $145\text{--}150^{\circ}/26\text{ mm.}$ (*p*-nitrobenzoate, m.p. $126\text{--}127^{\circ}$), converted by ozonisation and subsequent treatment with Zn dust into 2-hydroxy-3-methoxy-5-methylphenylacetaldehyde, m.p. 81° (oxime, m.p. 110° ; semicarbazone, m.p. 161° ; anil, m.p. 137°); this is transformed by the successive action of Zn dust in AcOH and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ in $\text{C}_5\text{H}_5\text{N}$ into the di-*p*-nitrobenzoate of 4-methyl-6- β -hydroxyethylguaiacol (I), m.p. $179\text{--}5^{\circ}$. 2 : 6 : 1- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ (improved prep. from *o*-vanillin) is converted similarly into 6-methylguaiacol allyl ether, b.p. $107\text{--}109^{\circ}/11\text{ mm.}$, isomerised to 6-methyl-4-allylguaiacol, b.p. $119\text{--}121^{\circ}/10\text{ mm.}$ This is ozonised to the non-cryst. 4-hydroxy-5-methoxy-3-methylphenylacetaldehyde (semicarbazone, m.p. 182°), which is reduced and then converted into the di-*p*-nitrobenzoate of 6-methyl-4- β -hydroxyethylguaiacol (II), m.p. $172\text{--}5\text{--}173\text{--}5^{\circ}$. Neither (I) nor (II) is identical with the di-*p*-nitrobenzoate of decarboxystyraxinic acid derived from egonol (III). The last substance must therefore be a coumarone and not a chromene derivative, in accordance with which decarboxystyraxinic acid (IV) gives veratric acid when methylated and then oxidised. Since (III) contains a primary OH but no asymmetric C, (IV) is 4- γ -hydroxypropylguaiacol (dihydroconiferyl alcohol) (V); this view is confirmed by direct comparison of the natural and synthetic di-*p*-nitrobenzoates, m.p. $121\text{--}121\text{--}5^{\circ}$ (also form, m.p. $113\text{--}113\text{--}5^{\circ}$), dibenzoates, m.p. $63\text{--}5\text{--}64\text{--}5^{\circ}$, and diphenylurethanes, m.p. $125\text{--}126^{\circ}$. Gradual addition of aq. KOH to (V) in boiling EtOH-CHCl_3 gives 2-hydroxy-3-methoxy-5- γ -hydroxy-*n*-propylbenzaldehyde, shown to be identical with styraxinaldehyde by comparison of the natural and synthetic semicarbazone, m.p. $188\text{--}5^{\circ}$ (decomp.), or, $+1\text{H}_2\text{O}$, m.p. $188\text{--}5^{\circ}$ (decomp.) after softening at $\sim 145^{\circ}$, phenylhydrazone, m.p. $152\text{--}5^{\circ}$, and aldazine, m.p. $185\text{--}5\text{--}186^{\circ}$. Acetylstyraxinaldehyde (semicarbazone, decomp. $214\text{--}214\text{--}5^{\circ}$) has two dimorphous forms, m.p. $97\text{--}98^{\circ}$ and 105° respectively. It is converted by H_2O_2 in AcOH at $60\text{--}65^{\circ}$ followed by hydrolysis into styroxinic acid. H. W.

Constitution of equol. F. WESSELY and F. PRILLINGER (Ber., 1939, 72, [B], 629—633; cf. A., 1938, II, 197).—Daidzein is hydrogenated to 7-hydroxy-3-*p*-hydroxyphenylchroman (I), m.p. 158° after softening at $156\text{--}5^{\circ}$ [*Me*₂ ether (II), m.p. 116° after softening at 114° ; diacetate (III), m.p. 128°], which cannot be compared directly with equol (IV) and its derivatives on account of the optical activity of the

latter. Attempted racemisation was unsuccessful and the resolution of the synthetic substances into their optical antipodes could not be effected by reason of the production of partial racemates. The ultraviolet absorption spectra of comparable natural and synthetic (IV) are not, however, identical but the more readily purified (II) and (III) are precisely similar, indicating that (IV) is (I). A possible alternative that (IV) is 6-hydroxy-2-*p*-hydroxyphenyl-2-methylcoumaran [obtained as racemate β -hydroxyphenyl- γ -2' : 4'-dihydroxyphenyl- Δ^{β} -propene (*loc. cit.*)] is disproved by the observations that 1 mol. of AcOH is obtained from it by oxidation with $\text{CrO}_3\text{-AcOH}$ whereas none is produced from equol Me_2 ether, and further that it always gives a small proportion of *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ and leaves a residue when sublimed in a high vac., whereas (IV) is stable under these conditions. H. W.

Identification of equol as 7-hydroxy-3-*p*-hydroxyphenylchroman. Synthesis of racemic equol methyl ether. (Miss) E. L. ANDERSON and G. F. MARRIAN (J. Biol. Chem., 1939, 127, 649—656; cf. Wessely *et al.*, A., 1938, II, 197).—Equol Me ether and CrO_3 in 90% AcOH at room temp. give a ketone, $\text{C}_{17}\text{H}_{16}\text{O}$, m.p. $120\text{--}5\text{--}121\text{--}5^{\circ}$ (sinters at 119°), $[\alpha]_{\text{D}}^{25} - 88\text{--}7^{\circ}$ in CHCl_3 , racemised by AcOH-HCl at 100° or Na_2CO_3 in hot 70% EtOH to the dl-ketone (I), m.p. $126\text{--}126\text{--}5^{\circ}$ (sinters at 125°), and reduced by Zn-Hg-AcOH-HCl to dl-equol Me ether, m.p. $112\text{--}5\text{--}114^{\circ}$ [sinters at 110° ; does not depress the m.p. of the l-ether (II); oxidised by CrO_3 to (I)]. *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$, *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, ZnCl_2 , and HCl in dry Et_2O give a ketimine and thence (hot N-HCl) 2-hydroxy-*p*-anisyl *p*-methoxybenzyl ketone, m.p. $102\text{--}5\text{--}104^{\circ}$, converted by HCO_2Et and Na in the cold into 7 : 4'-dimethoxyisoflavone, m.p. $158\text{--}159^{\circ}$; this resists Na-Hg and $\text{H}_2\text{-PtO}_2$ in EtOH , but with $\text{H}_2\text{-PtO}_2$ in AcOH rapidly gives 7 : 4'-dimethoxy-2 : 3-dihydroxyflavone = (I). Na-Hg reduces 7 : 4'-dimethoxyflavylium chloride to 7 : 4'-dimethoxy-2-phenylchroman, which depresses the m.p. of (II). R. S. C.

Dibenzfuran. VIII. Heteronuclear substitution. H. GILMAN, M. W. VAN ESS, and D. M. HAYES (J. Amer. Chem. Soc., 1939, 61, 643—648; cf. A., 1936, 208).—Bromination and nitration of Mo dibenzfuran-1-carboxylate (I) are proved to be heteronuclear. 1-Substituted dibenzfurans are readily obtained from 2 : 3 : 1- $\text{OAr}\cdot\text{C}_6\text{H}_3\text{X}\cdot\text{N}_2\text{Cl}$, but not from 2 : 1- $\text{C}_6\text{H}_4\text{X}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ or their substitution products. Li 1-dibenzfuryl and CO_2 give 34% of dibenzfuran-1-carboxylic acid and di-1-dibenzfuryl ketone, m.p. $172\text{--}173^{\circ}$. Conc. HNO_3 and (I) give the 7- (II), m.p. $156\text{--}158^{\circ}$, and usually some of the 6- (or, less probably, 8-) NO_2 -derivative (III), m.p. $205\text{--}205\text{--}5^{\circ}$, which are hydrolysed to 2-, m.p. $260\text{--}265^{\circ}$, and 6-nitrodibenzfuran-1-carboxylic acid, decomp. $300\text{--}305^{\circ}$, decarboxylated by Cu in quinoline to the known nitrodibenzfurans. *Me* xx-di-, m.p. $230\text{--}231^{\circ}$, and xxx-tri-nitrodibenzfuran-1-carboxylate, m.p. $208\text{--}210^{\circ}$, and a 1 : 1 compound, m.p. $170\text{--}172^{\circ}$, of (I) and (II) [or (III)], are also obtained. Br-CCl_4 at $60\text{--}70^{\circ}$ converts (I) into the 6-*Br*-derivative (IV), m.p. $166\text{--}167^{\circ}$, hydrolysed to the

6-Br-acid (V), m.p. 263—264°, which is decarboxylated by Cu-quinoline. 3 : 2 : 1-NO₂·C₆H₃Br·CO₂K [prep. from o-C₆H₄(CO₂H)₂ by way of the 3-NO₂- and its anhydro-2-hydroxymercuri-derivative] with p-C₆H₄Br·OK and Cu-bronze at 170° gives 2-nitro-6-carboxyphenyl p-C₆H₄Br ether, m.p. 167·5—168·5°, reduced by Sn-HCl to the NH₂-ether hydrochloride, m.p. 190—200° (decomp.); the diazo-compound thereof with 50% H₂SO₄ gives (V). With SnCl₂ in hot, conc. HCl-AcOH (II) gives Me 7-amino-dibenzfuran-1-carboxylate hydrochloride, decomp. 240°, which yields Me 7-acetamidodibenzfuran-1-carboxylate, m.p. 245—246°, converted by Br-AcOH into its 6-Br-derivative (VI), m.p. 247—247·5°. HNO₃ (d 1·5) converts (IV) into a (NO₂)₂-derivative, m.p. 259·5—260·5°, but HNO₃ (d 1·42) gives Me 6-bromo-7-nitrodibenzfuran-1-carboxylate (28%), m.p. 205—206°, reduced by SnCl₂-HCl-AcOH to the amine [gives (VI)] and hydrolysed to the corresponding acid, m.p. 331—334°, which with Cu-bronze in quinoline at 200—210° (or CuSO₄) gives 2-nitrodibenzfuran. 3-Bromo-2-nitrodibenzfuran similarly loses the Br when heated with Cu; the 7-Br-compound does not. The following synthesis is described:

$$o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc} \rightarrow 1 : 5 : 2\text{-C}_6\text{H}_3\text{MeBr}\cdot\text{NHAc} \rightarrow 3 : 1 : 5 : 2\text{-NO}_2\cdot\text{C}_6\text{H}_2\text{MeBr}\cdot\text{NHAc} \rightarrow 3 : 1 : 5 : 2\text{-NO}_2\cdot\text{C}_6\text{H}_2\text{MeBr}\cdot\text{NH}_2 \rightarrow 1 : 2 : 5 : 3\text{-C}_6\text{H}_3\text{MeBr}_2\cdot\text{NO}_2 \rightarrow \text{Ph } 5\text{-bromo-3-nitro-o-tolyl ether, m.p. } 92\text{--}94^\circ;$$

diazotisation and treatment with boiling 50% H₂SO₄ then gives 3-bromo-1-methyldibenzfuran, m.p. 106—106·5°, which is converted by H₂-Pd-CaCO₃ into 1-methyldibenzfuran, is stable to KMnO₄-NaOH, KMnO₄, dil. HNO₃ at 180°, and boiling aq. K₂Fe(CN)₆, and is either unaffected or destroyed by CrO₃.

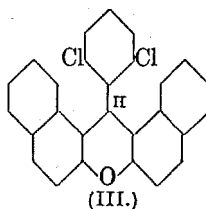
R. S. C.

Structure of rhodamines from their absorption spectra.—See A., 1939, I, 119.

Pyrenium compounds. XXXII. Dehydrenium dyes. II. W. DILTHEY, F. QUINT, and J. HEINEN (J. pr. Chem., 1939, [ii], 152, 49—98; cf. A., 1936, 1120).—Dehydrogenation of *ms*-aryldibenzoxanthenium salts (I) under the action of sunlight or of AlCl₃ is accompanied by an increase in the stability of the salts, the incidence of substantive dyeing properties (these two effects are inter-related), a marked bathochromic effect ascribed to compression of the ring systems, and maximal action of auxochromes if introduced in the *m*-position of the *ms*-Ph nucleus. The absorption spectra of the dehydrenium dyes at the visible end consist of several bands of very varying intensity and are considerably more complex than that of (I). OMe or NH₂ in the *m*-position in the *ms*-Ph nucleus displace the strong bands towards longer λ but do not influence the position of the weaker bands. Similarly placed NO₂ is weakly hypsochromic. Cl in the *p*-position has very little influence. Replacement of O of the pyran ring by S has a definitely bathochromic effect.

ms-Phenyldibenzoxanthenes are usually obtained from PhCHO which, in AcOH or EtOH containing strong acids as catalysts, smoothly condenses with 2 mols. of β-C₁₀H₇·OH whereby, as secondary change, the pyran ring is closed by loss of H₂O between the OH groups of β-C₁₀H₇·OH. CHPhCl₂ behaves

similarly but without the presence of acid, giving *ms*-phenyl-1 : 2 : 7 : 8-dibenzoxanthan (II), m.p. 190°, in 97% yield. Surprisingly,



(III.)

CPhCl₃ and β-C₁₀H₇·OH give a compound, m.p. 335°, which is probably [(C₁₀H₇·O)₂CPh]₂O since dinaphthol and CPh₂Cl₂ yield the substance, C₁₀H₆·O > CPh₂, m.p.

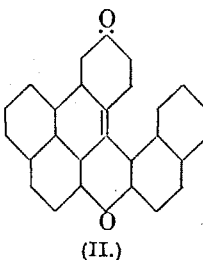
238°. Reaction occurs similarly in presence of AlCl₃. In boiling

EtOH the reactants yield (II) probably owing to the reduction of CPhCl₃ to CHPhCl₂ by EtOH. CHPhCl₂ does not appear to condense with 2 : 1-OH·C₁₀H₆·CO₂H or 1 : 2-C₁₀H₆Br·OH. 2 : 6-C₆H₃Cl₂·CHO and β-C₁₀H₇·OH afford 9·2' : 6'-dichlorophenyl-1 : 2 : 7 : 8-dibenzoxanthan (III), m.p. 264—265° [chloride; perchlorate, m.p. 293—295° (decomp.)]. Hot, conc. HNO₃ (d 1·4) converts (III) into a NO₂-derivative, which yields two perchlorates, C₂₉H₁₃O₅N₂Cl₃, orange, m.p. 308—312°, and C₂₇H₁₂O₁₁N₃Cl₃, yellow, m.p. 275—280°. 2 : 6-C₆H₃Cl₂·CHO and β-C₁₀H₇·SH give a compound, C₂₇H₁₈S₂Cl₂, which becomes glassy at 94—95° and darkens at >200°. 2 : 6-C₆H₃Cl₂·CHO when powerfully irradiated and treated with Cl₂ at 100° affords 2 : 6-C₆H₃Cl₂·COCl, b.p. 126—128°/18 mm. (corresponding amide, m.p. 198°). 5 : 2 : 6-NO₂·C₆H₂Cl₂·CHO and β-C₁₀H₇·OH in AcOH containing HCl at room temp. appear to yield 9-(?)·chloro-5-nitro-(?)·hydroxyphenyldibenzoxanthan, m.p. 246—247° (decomp.) [also + 1C₂H₅N; Ac derivative, C₂₉H₁₈O₅NCl, m.p. 318—320° (decomp.)]. 8 : 2-C₁₀H₆Cl·OH (prep. from 8 : 2-NH₂·C₁₀H₆·OH described) and PhCHO afford dichloro-*ms*-phenyldibenzoxanthan, m.p. 213—214·5°, dechlorinated by N₂H₄·H₂O and KOH in EtOH containing Pd-BaSO₄ to (II). Exposure of *ms*-o-nitrophenyldibenzoxanthenium perchlorate to sunlight causes removal of NO₂ and production of dehydro-*ms*-phenyldibenzoxanthenium perchlorate. Irradiation of 9·3'-nitrophenyl-1 : 2 : 7 : 8-dibenzoxanthenium perchlorate affords dehydro-9·3'-nitrophenyl-1 : 2 : 7 : 8-dibenzoxanthenium perchlorate. Fusion of *ms*-3'-nitrophenyldinaphthopyran with NaCl-AlCl₃ gives an amorphous, green hydrochloride, C₂₇H₁₆ONCl, and a black substance which is the product of its oxidation. 5 : 2-NO₂·C₆H₃Cl·CHO and β-C₁₀H₇·OH in AcOH containing HCl at room temp. give 2-chloro-5-nitrobenzylidenedi-β-naphthol, m.p. 240° (decomp.), cyclised by Ac₂O-H₂SO₄ in boiling AcOH to 9·2'-chloro-5'-nitrophenyl-1 : 2 : 7 : 8-dibenzoxanthan, m.p. 248°; the corresponding xanthenium perchlorate has m.p. 298°. Molten AlCl₃-NaCl converts the xanthan into a dehydro-*ms*-aminophenyldibenzoxanthenium compound [picrate, m.p. 270° (decomp.)], in which the presence of NH₂ is established by the wine-red halochromism with conc. H₂SO₄, the change of colour from blue to red (as a consequence of acetylation) when the solution in hot Ac₂O is treated with a little strong acid, and the similar change of colour when the solution is treated with PhCHO or *p*-OMe·C₆H₄·CHO or when NaNO₂ and HCl are added to the chloride dissolved in H₂O. *m*-OMe·C₆H₄·CHO and β-C₁₀H₇·OH give 3-methoxybenzylidenedi-β-naphthol, m.p. 203° or (+1AcOH) m.p. 157—159°, or at a higher temp. 9-*m*'-

anisyl-1 : 2 : 7 : 8-dibenzoxanthan, m.p. 176—177°; this is oxidised by MnO_2 in AcOH containing HCl to 9-3'-methoxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanol, m.p. 230—231° [perchlorate, m.p. 289° (decomp.) after softening at 282°; double salt, $\text{C}_{28}\text{H}_{19}\text{O}_3\text{Cl}_2\text{Fe}$, m.p. 222—224°]. Dehydro-9-m'-anisyl-dibenzoxanthanium perchlorate is also described. 9-p'-Anisyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate, m.p. 275°, could not be dehydrogenated by irradiation alone or with passage of air. Gradual addition of AlCl_3 to a mixture of BzCl and $(\beta\text{-C}_{10}\text{H}_7)_2\text{S}$ gives *ms*-phenyl-dibenzothioxanthanol, m.p. 240—241° (slight decomp.) [corresponding chloride, m.p. 180°; double salt with FeCl_3 , m.p. 255°; perchlorate, m.p. 295—296° (decomp.) after softening at 285—286°]. Reduction of the chloride by AcOH and a large excess of Zn dust affords 9-phenyl-1 : 2 : 7 : 8-dibenzothioxanthan, m.p. 230—231°. The carbinol is transformed by NaCl-AlCl_3 at 130—150° into dehydro-*ms*-phenyldibenzothioxanthanium chloride, decomp. >300° (corresponding perchlorate and picrate). *m*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ and $(\beta\text{-C}_{10}\text{H}_7)_2\text{S}$ afford *ms*-*m*-nitrophenyldibenzothioxanthanol, decomp. 305—306° after blackening, converted by NaCl-AlCl_3 at 120—150° into dehydro-*ms*-*m*-aminophenyldibenzothioxanthanium chloride (corresponding picrate). 2- $\text{C}_{10}\text{H}_7\text{-Ph}$, $\beta\text{-C}_{10}\text{H}_7\text{-OH}$, and PhCHO in boiling AcOH give 5 : 10-diphenyl-3 : 4 : 6 : 7-dibenzo-dihydroacridine, m.p. 303—304°, oxidised by MnO_2 and HCl in boiling Ac_2O to the carbinol, decomp. 278—279°. This is converted into the corresponding perchlorate, m.p. 325° (decomp.), and chloride, m.p. 199—200°; the salts pass when insolated or irradiated into dehydro-9 : 10-diphenyl-3 : 4 : 6 : 7-dibenzoacridinium chloride, m.p. 377—378° (decomp.) (in bath preheated to 350°) and m.p. ~380° (decomp.). 5-Phenyl-10-*p*-tolyl-3 : 4 : 6 : 7-dibenzodihydroacridine, m.p. 279—280°, is converted into 5-phenyl-10-*p*-tolyl-dibenzoacridanol, decomp. 242—243°. 5-Phenyl-10-*p*-tolyl-dibenzoacridinium perchlorate, m.p. 295—296° after softening and darkening, passes when irradiated into the dehydro-compound, isolated as the chloride, decomp. 385—386° (bath preheated to 350°). *p*- $\text{C}_6\text{H}_4\text{-Me-NH-C}_{10}\text{H}_7$, $\beta\text{-C}_{10}\text{H}_7\text{-OH}$, and *m*- $\text{OMe-C}_6\text{H}_4\text{-CHO}$ in boiling AcOH afford 5-*m*-anisyl-10-*p*-tolyl-dibenzodihydroacridine, m.p. 269—270° after softening and becoming discoloured, oxidised by PbO_2 in boiling PhCl to 5-*m*-anisyl-10-*p*-tolyl-dibenzodihydroacridanol, decomp. 285—286° after becoming discoloured at 260°, which passes into dehydro-5-*m*-anisyl-10-*p*-tolyl-dibenzoacridinium chloride [$\text{C}_{35}\text{H}_{26}\text{ON}^+\text{Cl}_3\text{HCl}\cdot 3\text{H}_2\text{O}$]. 1- $\text{C}_{10}\text{H}_7\text{-MgBr}$ and xanthone afford 9- α -naphthylxanthanol, m.p. 194—195° (decomp.), whence 9- α -naphthylxanthanium perchlorate, m.p. 274—275° after softening, which is unaltered by the light of the sun or of the Hg -vapour lamp. Anthraquinone-2-aldehyde, $\beta\text{-C}_{10}\text{H}_7\text{-OH}$, and AcOH containing conc. H_2SO_4 afford 9-2'-anthraquinonyl-xanthan, m.p. 273—274°, oxidised by MnO_2 in boiling AcOH to the corresponding xanthanol, m.p. 301—302° (decomp.), which yields 9-2'-anthraquinonyldibenzoxanthanium perchlorate, m.p. 324—325° (decomp.). H. W.

Pyrenium salts. XXXIII. Dehydrenium. III.
Action of auxochromes in the *meta* and *para*

positions of dehydrenium dyes. W. DILTHEY, F. QUINT, and H. STEPHAN (J. pr. Chem., 1939, [ii], 152, 99—113).—Auxochromes introduced into the *p*-position of the *ms*-Ph nucleus of dehydrenium dyes have a hypsochromic, in the *m*-position a bathochromic, effect. *p*- $\text{OBz-C}_6\text{H}_4\text{-CHO}$, new m.p. 90°, condenses with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ in AcOH saturated with HCl at room temp. to 4-benzoyloxyphenyldi-2'-hydroxy-1'-naphthylmethane, m.p. 213—214° (decomp.), or decomp. ~205° when slowly heated, converted by H_2SO_4 in boiling AcOH into 9-*p*-benzoyloxyphenyl-1 : 2 : 7 : 8-dibenzoxanthan, m.p. 277—278°, which is oxidised by PbO_2 in boiling AcOH to the corresponding xanthanol (I), decomp. ~270°. 9-*p*-Benzoyloxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate, m.p. 290—291° (decomp.), is transformed by NaOH-EtOH followed by HClO_4 into 9-*p*-hydroxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate, m.p. 320—321° (decomp.), the orange-red solution of which is scarcely dehydrogenated by prolonged exposure to sunlight. The corresponding *p*- $\text{OAc-C}_6\text{H}_4$ compound slowly passes under similar conditions into dehydro-9-*p*-acetoxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate. Extended exposure of (I) in EtOH containing HClO_4 to sunlight with frequent boiling of the solution gives dehydro-9-*p*-benzoyloxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate, m.p. 327—328° (decomp.), transformed by NaOH-EtOH into violone (II), m.p. >320°. This is immediately converted by HCl in AcOH or EtOH into dehydro-9-*p*-hydroxyphenyl-1 : 2 : 7 : 8-dibenzoxanthanium chloride and by PCl_5 in boiling PhNO_2 followed by HClO_4 into dehydro-9-*p*-chlorophenyl-1 : 2 : 7 : 8-dibenzoxanthanium perchlorate. Dehydro-9-*p*-aminophenyldibenzoxanthanium chloride, $\text{C}_{27}\text{H}_{17}\text{ONCl}_2$ (corresponding picrate), is obtained



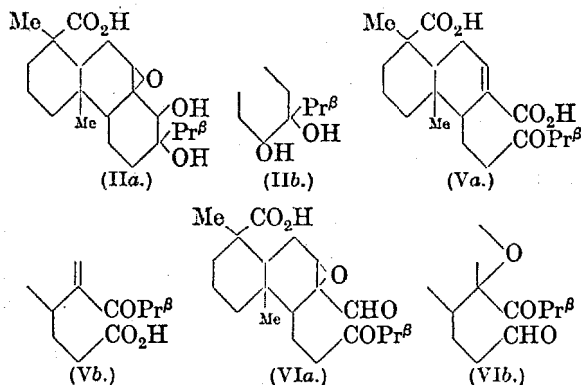
by fusion of the corresponding open NO_2 -carbinol with AlCl_3 . Addition of AlCl_3 to a solution of $(\beta\text{-C}_{10}\text{H}_7)_2\text{S}$ and *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ in CS_2 yields 9-*p*-nitrophenyl-1 : 2 : 7 : 8-dibenzothioxanthanol (III), decomp. 280° (bath preheated to 275°); this is converted in the usual manner into 9-*p*-nitrophenyldibenzothioxanthanium perchlorate, m.p. 292—293°. Fusion with NaCl-AlCl_3 transforms (III) into dehydro-9-*p*-aminophenyldibenzothioxanthanium chloride (corresponding perchlorate and picrate). H. W.

Pyrenium compounds. XXXIV. Structure of the dibenzoxanthenes. W. DILTHEY and H. STEPHAN (J. pr. Chem., 1939, [ii], 152, 114—125).— β -Dinaphthaxanthone (I), m.p. 194°, is transformed by MgPhBr into 9-phenyl-1 : 2 : 7 : 8-dibenzo-xanthanol, identical with that obtained by oxidation of the product obtained by condensing PhCHO with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$. (I) is therefore 1 : 2 : 7 : 8-dibenzo-xanthone. Addition of 2 : 3- $\text{C}_{10}\text{H}_6\text{Bz-OH}$ to 1- $\text{C}_{10}\text{H}_7\text{-MgBr}$ and treatment of the crude carbinol with boiling AcOH gives 9-phenyl-1 : 2 : 6 : 7-dibenzo-xanthan, m.p. 217—218° (II). This is oxidised (MnO_2 in warm AcOH containing HCl) and then transformed by HClO_4 into 9-phenyl-1 : 2 : 6 : 7-dibenzo-xanthanium perchlorate (II) m.p. 282° (decomp.),

whence 9-phenyl-1:2:6:7-dibenzoxanthanol (IV), m.p. 212—213° (slight decomp.). The dibenzoxanthone, m.p. 241°, is treated with MgPhBr and then converted into products identical with (II), (III), and (IV); it is therefore 1:2:6:7-dibenzoxanthone. These are the only dibenzoxanthones known, the compound, m.p. 149°, being identical with (I); confusion has been caused by a printer's error. Ziegler's product (A., 1922, i, 1047) is not the *lin.*-derivative but 9-styryl-1:2:6:7-dibenzoxanthone perchlorate. 2:3-C₁₀H₈Bz·OH is converted by 1:2-C₁₀H₆Me·MgI in PhMe into phenyl-2:1-methyl-naphthyl-3':2'-hydroxynaphthylcarbinol, m.p. 177—178° (decomp.), which could not be converted into the *lin.*-xanthan. Protracted boiling with AcOH in presence or absence of H₂SO₄, or heating with AcOH at 170°, causes merely slight resinification.

H. W.

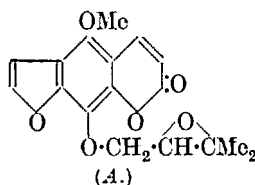
Constitution of abietic acid. Di-, tetra-, and chloro-hydroxyabietic acids, and their oxidation products. L. STERNBACH (Rocz. Chem., 1939, 19, 167—186).—Abietic acid is oxidised (KMnO₄ in KOH) to dihydroxyabietic acid (I) (*Me* ester, m.p. 106—107°) and its oxide (II), together with an isomeride (III), m.p. 130—150°, of tetrahydroxyabietic acid. (III) and HCl in COMe₂ give chlorotrihydroxy- (IV) and normal tetrahydroxy-abietic acid. (IV), treated with *n*-NaOH at 40°, yields (II), together with tetrahydroxyabietolactone, not melting at 330°, [α]_D²⁰ -75.8° ± 1.5° in CHCl₃. (II) or (III) in aq. COMe₂ at room temp. undergo gradual conversion into β-tetrahydroxyabietic acid, softening at 130°, m.p. 151°, [α]_D²⁰ -67.7° ± 0.4° in MeOH. (IV) is oxidised by CrO₃ in AcOH to a product, C₂₀H₃₁O₄Cl, m.p. 154—156° (semicarbazone, m.p. 204—206°). (I) is oxidised by Pb(OAc)₄ to a ketodicarboxylic acid (V), C₂₀H₃₀O₅, m.p. 212—212.5°, whilst an isomeric acid (VI), m.p. 132—134°, is obtained similarly from



(II). (II) is probably (IIa) or (IIb), (V) is (Va) or (Vb), and (VI) is (VIa) or (Vib). R. T.

Chemical constituents of umbelliferæ. VII. Constituents of the root of *Angelica glabra*, Makino. III. T. NOGUCHI and M. KAWANAMI (Ber., 1939, 72, [B], 483—489; cf. A., 1938, II, 375).—Byak-angelicol (I), m.p. 106°, [α]_D²⁰ +34.77° in C₅H₅N (*ibid.*, 153), contains 1 OMe but does not react with the customary CO₂ reagents. It is insol. in alkali hydroxide or carbonate and is not methylated

by CH₂N₂ and hence is neither acid nor phenol. Its lactone group is opened by hot dil. KOH with formation of isobyak-angelicol acid (II), C₁₆H₁₅O₈·OMe, m.p. 220°, [α]_D²⁰ +5.33° in C₅H₅N (*Me* ester, m.p. 125°; monoacetate, m.p. 200—201°). Oxidation of (I) by H₂O₂ in alkaline solution gives furan-2:3-dicarboxylic acid, m.p. 221°. The presence of a reactive double linking in (I) is established by its reduction by Na-Hg to dihydroisobyak-angelicol acid, C₁₇H₂₀O₇, m.p. 152° (acetate, m.p. 120°), also obtained from (II). Oxidation of (II) but not of (I) by HNO₃ yields (CH₂·CO₂H)₂. AcOH containing a little H₂SO₄ transforms (I) into 8-hydroxy-5-methoxypsoralene (III), m.p. 212°, methylated (CH₂N₂) to isopimpinellin and ethylated to 5-methoxy-8-ethoxypsoralene, m.p. 140—141°, thus establishing the nature of the fifth O. CrO₃ oxidises (I) to COMe₂, bergaptenquinone, and byak-angelicol acid, m.p. 227° [the *Me* ester is obtained synthetically from (III) and CH₂Cl·CO₂Me]. KMnO₄ transforms



(I) into OH·CMe₂·CO₂H. (I) is converted by P₂O₅ in boiling PhMe into anhydro-byak-angelicin, m.p. 107° (semicarbazone, m.p. 182°), by hydration with 1% H₂C₂O₄ into byak-angelicin, and by boiling 30% HCl-MeOH into byak-angelicol hydrochloride, m.p. 145°. (I) gives a diacetate, m.p. 118—119°, which does not depress the m.p. of byak-angelicin diacetate. (I) is therefore (A). H. W.

Chlorination of d-sesamin. T. KAKU, K. ITRYODA, and H. RI (Keijo J. Med., 1938, 9, 241—243).—*d*-Sesamin in "carbitol" with HCl and H₂O₂ (cold) yields 5:5'-dichlorosesamin, m.p. 191—192°, whilst at 100°, 4:5-dichloro-1:2-methylene-dioxybenzene, m.p. 79—80°, is formed, which with Cl₂ in AcOH yields successively 3:4:5-trichloro-, m.p. 114—115°, and 3:4:5:6-tetrachloro-1:2-methylene-dioxybenzene, m.p. 172—174°. J. D. R.

Dicyclic sulphonium salts with sulphur as branching atom. I. V. PRELOG and E. CERKOVNIKOV (Annalen, 1939, 537, 214—219; cf. A., 1938, II, 294, 457).—Gradual addition of Et α-c-dibromopentane-γ-carboxylate to K₂S-EtOH at 0° gives *Et* tetrahydro-1:4-thiopyran-4-carboxylate (*Et* pentamethylene sulphide 4-carboxylate), b.p. 118—120°/15 mm., hydrolysed by boiling 10% HCl to the free acid, m.p. 111.5—112.5° (amide, m.p. 184.5°; diethylamide, b.p. 113—115°/0.02 mm., m.p. 47.5—48.5°). The ester is reduced by Na-abs. EtOH to 4-hydroxymethyltetrahydro-1:4-thiopyran, b.p. ~138°/18 mm. (phenylurethane, m.p. 129—130°), very readily converted by conc. HCl into dicyclo-[1:2:2]-thianium-1-heptane chloride (cf. A.), m.p. 172° in a sealed capillary [corresponding platinichloride, m.p. 233—234°, and picrate, m.p. 274—275° (decomp.)]. The bromide, m.p. 272—273° in a sealed capillary, is converted by moist Ag₂O into the free base, which passes into a non-basic oil when its solution is evaporated at 60°. H. W.

Onium compounds. XX. Piperidinium analogues of choline and its homologues. R. R. RENSCHAW, M. ZIFF, B. BRODIE, and N. KORNBLUM (J. Amer. Chem. Soc., 1939, **61**, 638—640; cf. A., 1938, II, 396).—Et picolinate and Na-EtOH give 29% of 2-piperidylcarbinol, b.p. 80—83°/1 mm., 221° (decomp.)/760 mm. (picrate, m.p. 128—129.5°), which with MeI and Ba(OH)₂ in abs. EtOH yields 1:1-dimethyl-2-hydroxymethylpiperidinium iodide, m.p. 275—280° (decomp. from 200°) [corresponding chloride, m.p. 288° (decomp. from 200°); acetate, m.p. 126.5—128.5° (corr.)]. 1:1-Dimethyl-3-hydroxymethyl-, m.p. 140.5—142° (corr.) [corresponding chloride, m.p. 231—232° (decomp. from 200°); acetate, m.p. 134—135°], and 3- α -hydroxyethyl-piperidinium iodide, sinters at 132°, m.p. 137—139.5° (corr.) (acetate, m.p. 165—170°), are described. The acetates have rather weakly the acetylcholine action. R. S. C.

Piperidylethylbenzamidine.—See B., 1939, 356.

Pyridine derivatives.—See B., 1939, 437.

Behaviour of pyridine in binary systems with certain phenols and ketones. K. HRYNAKOWSKI and H. ELLERT (Rocz. Chem., 1939, **19**, 156—166).—The fusion diagrams suggest formation of 2:1 compounds in the systems: C₅H₅N-*o*-, m.p. 17°, -*m*-, and -*p*-C₆H₄(OH)₂, transition point (t.p.) 33°, and -*m*-NH₂·C₆H₄·OH, m.p. -9°, and 1:1 compounds in the systems C₅H₅N-*p*-C₆H₄(OH)₂, m.p. 78.2°, and -1:2:3-C₆H₃(OH)₃, t.p. 44.5°. Compounds are not formed in the systems C₅H₅N-*o*-C₆H₄(OMe)₂, -*o*-NH₂·C₆H₄·OH, -CHPh·CH·COMe, -benzil, and -COPhMe. R. T.

Direct synthesis of 3:5-di-iodopyridine. P. BAUMGARTEN (Ber., 1939, **72**, [B], 567—568).—The Na₂ salt of α -imino- ϵ -hydroxy- $\Delta^{8,9}$ -pentadiene-*N*-sulphonic acid suspended in MeOH is transformed by I into 3:5-di-iodopyridine, m.p. 171.5° [hydrochloride, m.p. 195—196° (decomp.)], with a little 3-iodopyridine. H. W.

Complex components of platinum and 2-aminopyridine. A. M. RUBINSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1938, **20**, 575—578).—2-Aminopyridine (I) and K₂PtCl₄ (2:1 mol.) yield the complex, PtCl₂·2(I), converted by Cl₂ into a complex, PtCl₄·2(C₅H₄Cl₂N·NH₂)₂, and by CS(NH₂)₂ and K₂C₂O₄ into Pt[4CS(NH₂)₂]C₂O₄·H₂O. Similarly, (I) and K₂PtCl₃·NO₂ and K₂Pt(NO₂)₄ give the complexes, PtClNO₂·2(I) and Pt(NO₂)₂·2(I) respectively. J. D. R.

Nitrones. IV. Carbenate zwitterions of the pyridinium series. F. KRÖHNKE (Ber., 1938, **72**, [B], 527—534).—Glyoxylanilide *p*-dimethylaminophenylnitron, m.p. 177° (decomp.), from anilinoformylmethylpyridinium bromide (I), is converted by 5*N*-H₂SO₄ into glyoxylanilide [phenylhydrazone (II), m.p. 171—172°]. (I) and PhNO afford glyoxylanilide phenylnitron, m.p. 149.5°, transformed by NHPh·NH₂ in EtOH into (II). Anilinothioformylmethylpyridinium perchlorate, *p*-NO·C₆H₄·NMe₂, and *N*-NaOH in EtOH give thioglyoxylanilide *p*-dimethylaminophenylnitron, m.p. 150—151°, converted by successive treatments with 5*N*-H₂SO₄ and NHPh·NH₂ into thioglyoxylanilide phenylhydrazone, decomp. ~170°.

CH₂Br·CO·NH₂ and C₅H₅N in C₆H₆ give aminoformylmethylpyridinium bromide, m.p. 200° (corresponding perchlorate, m.p. 136°), which with *p*-NO·C₆H₄·NMe₂ and piperidine in EtOH affords glyoxylanilide *p*-dimethylaminophenylnitron, decomp. ~178°. CH₂Br·CO·NH₂ and isoquinoline give aminoformylmethylisoquinolinium bromide, m.p. 203°. α -Anilinoformylethylpyridinium bromide, m.p. 220° (corresponding perchlorate, m.p. 219°), is transformed into the *p*-dimethylaminophenylnitron, m.p. 175° (decomp.), hydrolysed to pyruvanilide. Phenylbromoacetanilide, m.p. 146°, is transformed into the corresponding pyridinium bromide, m.p. 114°, which gives benzoylformanilide *p*-dimethylaminophenylnitron, form A, m.p. 175°, form B, m.p. 168° (decomp.), either of which is hydrolysed by 5*N*-H₂SO₄ to PhCO·NHPh. Cyanobenzylpyridinium bromide, *p*-NO·C₆H₄·NMe₂, and *N*-NaOH in EtOH yield benzoyl cyanide *p*-dimethylaminophenylnitron, red plates, m.p. 140—142°, and hexagonal orange crystals, m.p. 186.5°. Desylpyridinium bromide and PhNO give benzil phenylnitron, m.p. 156°, hydrolysed to benzil. H. W.

Synthesis of 2:3-derivatives of pyridine. P. BAUMGARTEN and A. DORNOW (Ber., 1939, **72**, [B], 563—566).—Et β -aminocrotonate and OEt·CH:CH·CH(OEt)₂ (I) at 100° afford *Et* 2-methylpyridine-3-carboxylate, b.p. 118°/20 mm. (picrate, m.p. 146—147°), in ~30% yield. It is hydrolysed to 2-methylpyridine-3-carboxylic acid, m.p. 226—227°, the hydrochloride, m.p. 226°, of which is transformed by SOCl₂ followed by NHEt₂·HCl at 150—160° into 2-methylnicotindithiethylamide, b.p. 167°/12 mm., m.p. ~30°. β -Aminocrotononitrile and (I) slowly afford 3-cyano-2-methylpyridine, m.p. 58° (picrate, m.p. 170°). Acetylacetoneimine and (I) yield 3-acetyl-2-methylpyridine, b.p. 99—100°/15 mm., m.p. 30—31° (picrate, m.p. 174°), 3-Benzoyl-2-methylpyridine, b.p. 165°/10 mm. (perchlorate, m.p. 175°), is described. H. W.

Nitration of methyl homologues of pyridine. E. PLAZEK (Ber., 1939, **72**, [B], 577—581).—Introduction of Me at C₍₂₎ or C₍₄₎ facilitates the nitration of C₅H₅N; the effect increases with the no. of Me which are introduced. Gradual addition of KNO₃ to 2:4:6-trimethylpyridine in fuming H₂SO₄ (18% SO₃) at 100° gives within 5 hr. an almost quant. yield of 3-nitro-2:4:6-trimethylpyridine, b.p. 229°/733 mm., m.p. 38° (picrate, m.p. 175°). This is reduced by SnCl₂ and conc. HCl to 3-amino-2:4:6-trimethylpyridine, b.p. 244°/744 mm., m.p. 66° (picrate, m.p. 201°), whence 3-hydroxy-2:4:6-trimethylpyridine, m.p. 137°. Under similar conditions but with H₂SO₄ containing 28% of SO₃, 2:6-dimethylpyridine affords 3-nitro-2:6-dimethylpyridine, b.p. 227°/738 mm., m.p. 37° (picrate, m.p. 143°), in ~66% yield. This is reduced (SnCl₂ and HCl) to 3-amino-, b.p. 230°/738 mm., m.p. 124° (picrate, m.p. 181°), whence 3-hydroxy-, m.p. 209°, 2:6-dimethylpyridine. Rapid addition of KNO₃ to 2-methylpyridine in fuming H₂SO₄ (18% SO₃) at 160—180° gives a very small yield of 5-nitro-2-methylpyridine, m.p. 112° (picrate, m.p. 132°). This yields 5-amino-2-methylpyridine, m.p. 96° (picrate, m.p. 201°; Ac derivative, m.p. 126°). H. W.

Alphylcarbamatomethylpyridinium salts.—See B., 1939, 357.

8-Amino-6-methoxyquinoline and its derivatives. A. TSCHITSCHIBABIN and C. HOFFMANN (Compt. rend., 1939, 208, 525—527).—8-Amino-6-methoxyquinoline (*benzoate*, m.p. 157°, stable in cold dil. HCl; *benzyl*-, m.p. 65°, *p*-nitrobenzyl-, m.p. 135°, *benzhydryl*-, m.p. 160°, and *-cinnamyl-amino*-, m.p. 96°, derivatives which do not give salts with cold mineral acids but when warmed, regenerate the parent base) is purified by fractional crystallisation of the hydrochloride, m.p. 52° (lit., 41.5°), hydrobromide, or sulphate. 8- δ -Diethylaminoisoamylamino-6-methoxyquinoline (I) (plasmaquine), b.p. 203—205°/3 mm., with picric acid in hot EtOAc affords a *dipicrate*, m.p. 128—137°. 8- γ -Diethylaminopropylamino-6-methoxyquinoline (III) (rhodoquine), b.p. 201—203°/3 mm., is purified through its dihydriodide, m.p. 215° (block) (lit., 208°), and *dipicrate*, m.p. 190° (block). The salts of (I) and (III) with HIO_3 give blue-violet and red-violet colours, respectively. J. L. D.

Preparation and therapeutic properties of certain 4-substituted quinoline derivatives. W. L. GLEN, M. M. J. SUTHERLAND, and F. J. WILSON. **Antiseptic properties and trypanocidal action.** C. H. BROWNING, P. BROWNING, and J. V. M. ROBB (J.C.S., 1939, 489—492).—By heating 4-chloro-2-methylquinoline with the appropriate amine, and condensing the product or its quaternary salt with an aldehyde, using $\text{C}_5\text{H}_{11}\text{N}$ as catalyst, the following have been prepared: 4-*anilino*-2-methylquinoline *methochloride*, m.p. 259—261°; 4-*p*-acetamidoanilino-2-methylquinoline, m.p. 280—285° [*methiodide*, m.p. 270—284° (decomp.); *methochloride*, m.p. 278—285° (decomp.)]; 4-*anilino*-2-dimethylaminostyrylquinoline *methiodide*, m.p. 250—260° (decomp.) [*methochloride*, m.p. 280—285° (decomp.)]; 4-*p*-acetamidoanilino-2-*p*-dimethylaminostyrylquinoline *methiodide*, m.p. 270—275° (decomp.) (*methochloride*, m.p. above 310°); 2 : 2'-dimethyl-4 : 6'-diquinolylamine, m.p. ~110° [*dimethiodide*, m.p. 230—275° (decomp.)]; 2 : 2'-bis-*p*-dimethylaminostyryl-4 : 6'-diquinolylamine *dimethiodide*, m.p. 230—255° (decomp.); and *p*-acetamidoanilino-2-*p*-dimethylaminoanilinomethylquinoline *methiodide*, m.p. indefinite. The results of examination for antiseptic properties *in vitro* and trypanocidal action *in vivo* are described.

F. R. S.

Quinoline derivatives (antimalarials).—See B., 1939, 438.

6-Methyl-1-ethyl-2-quinolinyldenepentamethine- ω -aldehyde.—See B., 1939, 357.

New general synthesis of 1-isoquinoline derivatives. W. DAVIES, J. F. KEFFORD, and J. L. OSBORNE (J.C.S., 1939, 360—361).—*trans*- ω -Bromocyanostyrene and MgMeI , MgPhBr , and CH_2PhMgBr give respectively small yields of 1-methyl-, 1-phenyl-, and 1-benzyl-isoquinoline, with loss of Mg halogenobromide. ω -Bromo-*o*-acetyl- (2 : 4-dinitrophenyl)hydrazones, m.p. 182°, -benzoyl- (2 : 4-dinitrophenyl)hydrazones, m.p. 206—207°, and -phenylacetylstyrene (2 : 4-dinitrophenyl)hydrazones, m.p. 162.5° are formed as by-products. F. R. S.

Preparation of nitro- and amino-derivatives of carbazole. R. K. EICHMAN, V. O. LUKASCHEVITSCH, and E. A. SILAIEVA (Prom. Org. Chim., 1939, 6, 93—95).—Detailed directions for prep. and purification of 3-nitrocarbazole (I) via the *N*-NO-derivative are given. (I) in AcOH is nitrated at 70°, to yield 3 : 6-dinitrocarbazole, m.p. 360°. This is reduced (Na_2S) to the 3 : 6-diamino-compound [Bz_2 derivative, m.p. 281° (lit. 270°)]. R. T.

Carbazole derivatives. II. N. B. EDDY (J. Pharm. Exp. Ther., 1939, 65, 308—317).—See A., 1939, III, 508. The following are described, without details of prep.: 9-methyl-2- γ -dimethyl-, m.p. 96.5—99° [*hydrochloride*, m.p. 195—196.2° (decomp.)], and -diethyl-amino-, m.p. 76.8°, and -tetrahydroisoquinolino-, m.p. 151—153°, - α -hydroxy-*n*-propylcarbazole; 1-hydroxy-, m.p. 118.5°, and 1-hydroxy-9-methyl-2-dimethylaminomethyl-, m.p. 123.5°, -1 : 2 : 3 : 4-tetrahydrocarbazole.

Sulphonation of 5 : 6-benzoquinoline. J. BÖHM (Rocz. Chem., 1939, 19, 109—115).—5 : 6-Benzoquinoline and 20% oleum at 100° (2 hr.) yield 5 : 6-benzoquinoline-3'- and -5'-sulphonic acid, together with small amounts of a third, unidentified acid, decomp. 369—378°. The products were identified by conversion into the corresponding phenols. 3'-Amino- and 3'-hydroxy-5 : 6-benzoquinoline have m.p. 175.5—176.5° (lit. 158°) and 245—247° (lit. 208—211°). R. T.

Acridine derivatives. II. B. S. DUEGAN, K. S. NARANG, and J. N. RAY (J.C.S., 1939, 476—478; cf. A., 1938, II, 203).—5-Chloro-3-nitro-7-methoxyacridine and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ give 3-nitro-5-*p*-amidosulphonylanilino-7-methoxyacridine, m.p. 304° (decomp.), reduced to the 3- NH_2 -compound [*hydrochloride*, m.p. 315° (decomp.)]; *Ac* derivative, m.p. 185°. 3-Nitro-5- β -hydroxy-, m.p. 237° (decomp.), obtained from 5-chloro-3-nitro-7-methoxyacridine and $\text{OH}\cdot[\text{CH}_2]_2\text{NH}_2$, with SOCl_2 forms the - β -chloro-compound, m.p. 191°, converted into the -piperidinoethylamino-7-methoxyacridine, m.p. 171° (decomp.), which is reduced to 3-amino-5- β -piperidinoethylamino-7-methoxyacridine, m.p. 170° (decomp.) (*Ac* derivative, m.p. 206°). The corresponding OEt-compounds are 3-nitro-5- β -hydroxy-, m.p. 226° (decomp.), -chloro-, m.p. 176° (decomp.) and -piperidino-, m.p. 221° (decomp.), and 3-amino-5- β -piperidinoethylamino-7-ethoxyacridine, m.p. 180°. 3-Nitro-, m.p. 155° (decomp.), is reduced to 3-amino-5- β -diethylaminoethylamino-7-methoxyacridine, m.p. 128—134° (decomp.). 3-Nitro-5-*p*-anisidino-7-ethoxyacridine [*hydrochloride*, m.p. 315° (decomp.)] is reduced to the 3-amino-compound, m.p. 168° (*Ac* derivative, m.p. 257°), and 3-amino- [*Ac* derivative, m.p. 193° (decomp.)] is similarly obtained from 3-nitro-5-*n*-butylamino-7-ethoxyacridine [*hydrochloride*, m.p. 265° (decomp.)]. F. R. S.

Polynuclear, condensed systems with heterocyclic rings. IV. W. BORSCHÉ and H. HAHN (Annalen, 1939, 537, 219—245).—4-Phenyl-2 : 6-dimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylic acid is converted by successive treatments with SOCl_2 and $\text{AlCl}_3\text{-PhNO}_2$ into 1 : 3-dimethyl-2-*aza*-

fluorenone (I), m.p. 154—155° [picrate, decomp. 234°; methiodide, m.p. 225—227° (decomp.); oxime, m.p. 280—281° (decomp.); 2:4-dinitrophenylhydrazine, m.p. 307° (decomp.)], converted by $N_2H_4 \cdot H_2O$ at 200° into 1:3-dimethyl-2-azafluorene, m.p. 85—86°. $CH_3Ac \cdot CO_2Et$, $Et \beta$ -aminocrotonate (II), and $p\text{-OMe} \cdot C_6H_4 \cdot CHO$ yield Et_2 4-p-anisyl-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate (III), m.p. 157°, oxidised by CrO_3 to Et_2 4-p-anisyl-2:6-dimethylpyridine-3:5-dicarboxylate, m.p. 48—49°. (III) is boiled under atm. pressure and then hydrolysed to 4-p-anisyl-2:6-dimethylpyridine-3-carboxylic acid, m.p. ~230° (*Cu* salt), transformed by the successive action of $SOCl_2$ and $AlCl_3 \cdot PhNO_2$ into 7-methoxy-1:3-dimethyl-2-azafluorenone (picrate, decomp. 237°; methiodide, decomp. 238—240°; oxime, decomp. 283—284°), which gives 7-methoxy-1:3-dimethyl-2-azafluorene, m.p. 118—120°. $CH_3Ac \cdot CO_2Et$, (II), and piperonal yield Et_2 4:3':4'-methylenedioxyphenyl-2:6-dimethyl-dihydropyridine-3:5-dicarboxylate, m.p. 134°, which gives 4:3':4'-methylenedioxyphenyl-2:6-dimethylpyridine-3-carboxylic acid, m.p. ~250° (*Cu* salt), converted into 6:7(7:8)-dihydroxy-1:3-dimethyl-2-azafluorenone, m.p. 255° (decomp.). Et_2 methylenedibenzoylacetate is heated with NH_4OAc at 170—180° and the product, b.p. ~250°/12 mm., is oxidised to Et_2 2:6-diphenylpyridine-3:5-dicarboxylate, hydrolysed to 2:6-diphenylpyridine-3:5-dicarboxylic acid, m.p. 283° (decomp.), which is decarboxylated by Cu -bronze to 2:6-diphenylpyridine, m.p. 81°. The acid (*dianilide*, m.p. 285°) is transformed by $SOCl_2$ into the chloride, m.p. 127°, cyclised by $AlCl_3$ in $PhNO_2$ to 2:3:5:6-dibenzoylenepyridine, m.p. 257°; this is very smoothly reduced by $N_2H_4 \cdot H_2O$ to 2:3:5:6-dibenzoylenepyridine, m.p. 206—207°. Et_2 styryl-lutidinedicarboxylate is hydrolysed to the corresponding *Et H* compound (IV), m.p. 184—185°, which loses CO_2 at ~230° giving *Et* 4-styryl-2:6-dimethylpyridine-3-carboxylate, b.p. 240—245°/14 mm. (picrate, m.p. 190—191°). This is hydrolysed to the free acid, m.p. 253°, transformed by $SOCl_2$ into the corresponding chloride (whence the *anilide*, m.p. 133° after softening at 129°), which could not be cyclised satisfactorily. (IV) is hydrogenated ($Pd-C$ in $AcOH$) and subsequently decarboxylated to *Et* 4- β -phenylethyl-2:6-dimethylpyridine-3-carboxylate (picrate, m.p. 132—133°); the free acid, m.p. 183—186°, yields a chloride, transformed by $AlCl_3$ in $PhNO_2$ into a dark brown resin of high m.p. which could not be caused to crystallise. 1-Phenylpyrazole-5-carboxyl chloride is little affected by $AlCl_3$ in warm $PhNO_2$ but is transformed by $AlCl_3$ and C_6H_6 into 5-benzoyl-1-phenylpyrazole, m.p. 119—120° (2:4-dinitrophenylhydrazine, m.p. 194—195°). Deoxybenzoin, $Et_2C_2O_4$, and $KOEt$ in $EtOH \cdot Et_2O$ afford *Et* desylglyoxylate (V), m.p. 106—107°, converted by $N_2H_4 \cdot H_2O$ in $MeOH$ into *Et* diphenylpyrazolecarboxylate, m.p. 195—197° (*Ac* derivative, m.p. 189—190°), and an isomeric compound, m.p. 158—159° (*Ac* derivative, m.p. 150—151°). Either ester is hydrolysed by $KOH \cdot EtOH$ to 3:4-diphenylpyrazole-5-carboxylic acid, m.p. 261° (*Et* ester, m.p. 158°), which passes above its m.p. into 3:4-diphenylpyrazole,

m.p. 154°, and is quantitatively converted by $SOCl_2$ into the diketopiperazine (VI), m.p. 346°; this is transformed by N_2H_4 at 200° into a diphenylpyrazoline, m.p. 176—177°, and a substance, $(C_6H_5N_2)_2$, m.p. 320—321°. $NHPh \cdot NH_2$ and (V) at 100° give mainly the α -phenylhydrazone, m.p. 133°, of (V) with some *Et* 1:4:5-triphenylpyrazole-3-carboxylate, m.p. 158°, hydrolysed to the free acid, m.p. 248°. 1:4:5-Triphenylpyrazole-3-carboxyl chloride, m.p. 155° (corresponding *anilide*, m.p. 205—206°), does not appear to be affected by $AlCl_3$ in $PhNO_2$ but with $AlCl_3$ in C_6H_6 gives 3-benzoyl-1:4:5-triphenylpyrazole, m.p. 155° (2:4-dinitrophenylhydrazine, m.p. 210—212°). Production of a tricyclic ketone could not be effected by treating 1:5-diphenyl-3-methylpyrazole-4-carboxylic acid with conc. H_2SO_4 or from its chloride and $AlCl_3$ in $PhNO_2$. 4-Benzoyl-1:5-diphenyl-3-methylpyrazole (2:4-dinitrophenylhydrazine, m.p. 207°) has m.p. 115—116°. *Et* α -phenylacetylacetoacetate and $NHPh \cdot NH_2$ give mainly *Et* 1-phenyl-5(or 3)-benzyl-3-(or 5)-methylpyrazole-4-carboxylate (with phenylacetphenylhydrazine, m.p. 173—174°); the free acid, m.p. 178°, gives a chloride (corresponding *anilide*, m.p. 203°) which becomes resinified when cyclisation in $PhNO_2$ is attempted but with $AlCl_3$ and C_6H_6 affords the ketone, $o\text{-}C_6H_4 \cdot \begin{matrix} CO-C \cdot CMe \\ | \\ CH_2 \cdot C \cdot NPh \end{matrix} \cdot N$, m.p. 236—238°. 1-Phenyl-3-benzylpyrazol-5-one, m.p. 135—136°, and diazotised $p\text{-}C_6H_4Me \cdot NH_2$ afford 4'-tolueneazo-1-phenyl-3-benzylpyrazol-5-one, m.p. 164°. 1-Phenylpyrro-2:3-diazole-5-carboxylic acid gives a non-cryst. chloride (corresponding *anilide*, m.p. 168°), which with $AlCl_3$ and C_6H_6 gives 5-benzoyl-1-phenylpyrro-2:3-diazole, m.p. 100—101°, in 10% yield and with $PhMe$ affords 5-toluoyl-1-phenylpyrro-2:3-diazole, m.p. 122—123°, in 65% yield; this gives two 2:4-dinitrophenylhydrazones, m.p. 242—244° and 205° respectively. 1:5-Diphenylpyrro-2:3-diazole-4-carboxyl chloride is not cyclised by $AlCl_3$ in $PhNO_2$ but with $AlCl_3$ in C_6H_6 yields 4-benzoyl-1:5-diphenylpyrro-2:3-diazole, m.p. 165—166° (2:4-dinitrophenylhydrazine, m.p. 230—234°). 5-Benzyl-1-phenylpyrro-2:3-diazole-4-carboxylic acid, m.p. 150—151° (chloride; *anilide*, m.p. 189°), passes at 155° into CO_2 and 5-benzyl-1-phenylpyrro-2:3-diazole, m.p. 70—71. 5-Benzyl-1-phenylpyrro-2:3-diazole-4-carboxyl chloride is quantitatively converted by $AlCl_3$ and C_6H_6 into 4-hydroxy-1-phenyl-1:2:3-triaza-5:6-benzoindene [4-hydroxy-1-phenylaphthotriazole], m.p. 216° (decomp.) (*Ac* derivative, m.p. 126—127°), oxidised by $Na_2Cr_2O_7$ to 1-phenyl-1:2:3-triaza-5:6-benzoindene-4:7-quinone, m.p. 242—243°. The 2:4-dinitrophenylhydrazone of $CH_2Ph \cdot CO \cdot CH_2 \cdot CO_2Et$ has m.p. 155°.

H. W.

Chloro-compounds obtained by means of aqueous sodium hypochlorite. A. LEULIER and R. COHEN (*J. Pharm. Chim.*, 1939, [viii], 29, 245—251).— $(CH_2)_6N_4$ (I) with aq. $KHCO_3$ and $NaOCl$ affords NN' -dichlorohexamethylenetetramine, decomp. slowly at 77° (block) and rapidly at 140°, which decomposes in air to give the hydrochloride of (I),

NH_4Cl , and NH_3MeCl . Piperazine similarly affords *NN*-dichloropiperazine, m.p. 74° (block), which when warmed with As_2O_3 gives CH_2O . Antipyrine similarly affords chloroantipyrine, m.p. $131\text{--}132^\circ$ (lit., $126\text{--}127^\circ$). The properties of these compounds are described.

J. L. D.

Relationship of the structure of *l*-carnosine to its depressor activity. M. HUNT and C. DU VIGNEAUD (J. Biol. Chem., 1939, 127, 727—735).—In order to have depressor activity carnosine analogues must have the correct spatial configuration and the NH_2 on $\text{C}_{(6)}$ of the acyl moiety, the $\text{C}_{(6)}$ of the acyl moiety must not carry an alkyl, and the NH_2 of the acyl moiety must be attached to a primary C. *dl*- β -Amino-*n*-butyric acid is best isolated as its *carbobenzyloxy*-derivative, m.p. 126° , resolved by *d*- and *l*- $\text{CHPhMe}\cdot\text{NH}_2$ into the *d*- and *l*-salts, m.p. 114° , which yield the *d*- and *l*-*carbobenzyloxy*-acids (A), m.p. 110° . Hydrogenation yields *d*- and *l*- $\text{NH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $[\alpha]_D^{25} +34^\circ$, -34.5° in H_2O . The chlorides of (A) with histidine Me ester give *carbobenzyloxy*-*d*-, m.p. 204° , $[\alpha]_D^{25} +28^\circ$ in H_2O , and *l*- β -amino-*n*-butyryl-*l*-histidine, m.p. 207° , $[\alpha]_D^{25} +17^\circ$ in H_2O , converted as sulphates by $\text{H}_2\text{--Pd-black}$ in H_2O into *d*-, m.p. 260° , $[\alpha]_D^{25} +21^\circ$ in H_2O , and *l*- β -amino-*n*-butyryl-*l*-histidine (B), m.p. 260° , $[\alpha]_D^{25} +8.4^\circ$ in H_2O . $\text{CHMeBr}\cdot\text{CO}_2\text{Na}$ and aq. NaCN at 60° give the nitrile, hydrogenated (Raney Ni) to the NH_2 -acid, isolated as *carbobenzyloxy*-*dl*- β -amino-isobutyric acid, m.p. 76° , which by the methods given above yields *carbobenzyloxy*-*d*-, m.p. 88° , $[\alpha]_D^{25} -6^\circ$ in H_2O (*l*- $\text{CHPhMe}\cdot\text{NH}_2$ salt, m.p. 98°), and *l*- β -amino-isobutyric acid, m.p. 88° , $[\alpha]_D^{25} +6^\circ$ in H_2O (*d*- $\text{CHPhMe}\cdot\text{NH}_2$ salt, m.p. 98°), *d*-, $+2\text{H}_2\text{O}$, m.p. 135° , $[\alpha]_D^{25} +18^\circ$ in H_2O (Cu salt, m.p. 230°), and *l*- β -aminoisobutyryl-*l*-histidine (C), m.p. 240° , $[\alpha]_D^{25} +2^\circ$ in H_2O (Cu derivative, m.p. 205°) (*carbobenzyloxy*-derivatives, oils). (B) and (C) have no depressor activity, even in large doses.

R. S. C.

Pyrimidines. Molecular rearrangement of 2-chloro-6-thiocyanopyrimidine to the [thio] carbimide. Y. F. CHI and Y. H. CHEN (J. Chem. Eng. China, 1938, 5, 35—39).—Prep. of uracil is modified to give a 58% yield. 2:6-Dichloropyrimidine and KCNS in hot EtOH give 2-chloro-6-thiocyanopyrimidine (I), m.p. $125\text{--}126^\circ$ (stable to aq. NH_3), and ethyl-2-chloro-6-pyrimidylthiourethane, m.p. $259\text{--}261^\circ$ (decomp.). With $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ at 100° (I) gives acetyl-2-chloro-6-pyrimidylthiourethane, m.p. $283\text{--}284^\circ$. In C_6H_6 at 170° or alone at $130\text{--}210^\circ$ (I) gives the thiocarbimide, converted by NH_2Ph into *N*-phenyl-*N'*-2-chloro-6-pyrimidylthiocarbamide, m.p. $200\text{--}201^\circ$, by aq. NH_3 into 2-chloro-6-pyrimidylthiocarbamide, m.p. $316\text{--}318^\circ$, and by EtOH into ethyl-2-chloro-6-pyrimidylthiourethane, m.p. $260\text{--}261^\circ$, which is also obtained directly from (I) by EtOH at 100° .

R. S. C.

Geometrical isomerism of indigotin. J. VAN ALPHEN (Ber., 1939, 72, [B], 525—526).—Oxalyl-indigotin can be obtained from $(\text{COCl})_2$ and indigotin (I) in $\text{C}_5\text{H}_5\text{N}$ at room temp. whereas no reaction occurs with $\text{CH}_2\text{Ph}\cdot\text{COCl}$ under these conditions. Arguments are advanced in favour of the view that (I) is a resonance hybrid.

H. W.

Phenanthrolines.—See B., 1939, 357.

Safranines.—See B., 1939, 359.

Pyrazoleanthrones.—See B., 1939, 359.

Constitution of pharmacologically useful purine derivatives in solution. W. PAUL (Arch. Pharm., 1939, 277, 105—116).—The rates of dialysis of mixtures prove absence of compounds of Na theobromine with Na salicylate, benzoate, or acetate in H_2O , but indicate hydration; variations in the degree of hydration may explain the mutual pharmacological effects of the drugs.

R. S. C.

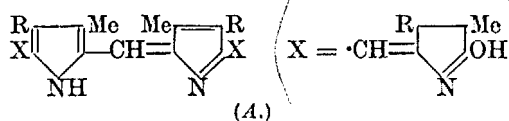
Separation of lactoflavin (vitamin- B_2) and lactoflavin phosphate. A. EMMERIE (Rec. trav. chim., 1939, 58, 290—292; cf. A., 1938, III, 414).—Lactoflavin is rapidly extracted from aq. solutions containing lactoflavin phosphate (only small quantities extracted) by $\text{CH}_2\text{Ph}\cdot\text{OH}$, $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{OH}$, $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{OH}$, or $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CMeEt}\cdot\text{OH}$.

A. T. P.

Bile acids. XXII. Synthesis of vinyl-substituted bilirubin derivatives. H. FISCHER and H. REINECKE (Z. physiol. Chem., 1939, 258, 9—15; cf. A., 1939, II, 186).—Bilirubin boiled for 15 sec. with resorcinol gives 20% of 5-hydroxy-4:3'-dimethyl-3-vinylpyrromethene-4'-propionic acid (I), m.p. 245° [Me ester (II), m.p. 185° ; azo-dye, sinters 205° , does not melt below 360° , from (II) and PhN_2Cl]. When the duration of boiling is 30 sec., a substance which yields a Me ester (III), m.p. 190° , probably Me vinyl-neoxanthobilirubinate-IV, is obtained. (III) does not yield methylethylmaleimide on oxidation and with $\text{CH}_2\text{O}\cdot\text{HCl}$ it gives a substance, m.p. 280° . (I) in 0.1N-NaOH is reduced (colloidal Pd- H_2) to neobilirubinic acid, 2 H_2 being taken up. If the hydrogenation is interrupted when H_2 has been taken up, neoxanthobilirubinic acid is obtained. With $\text{CH}_2\text{O}\cdot\text{HCl}$ (I) yields 1':8'-dihydroxy-1:3:6:8-tetramethyl-2:7-divinylbilidiene-(2'- α -7'- γ)-4:5-dipropionic acid, m.p. 312° , and with Me formylisoneoxanthobilirubinate in boiling MeOH containing HBr it yields *Me*, 1':8'-dihydroxy-1:3:6:7-tetramethyl-8-ethyl-2-vinyl-bilitriene-(2'- α -4'-ms)-4:5-dipropionate, m.p. 225° .

W. McC.

Bile pigments. XXIII. Dimethoxy- and dihalogeno-dipyrromethenes and their reactions. H. FISCHER and A. STACHEL (Z. physiol. Chem., 1939, 258, 121—136; cf. A., 1935, 363).—5-Bromo-5'-methoxy-4:4'-dimethyl-3:3'-di-(β -carboxyethyl)-pyrromethene (I) (Zn salt, m.p. 134° , of Me₂ ester) with 40% CH_2O and conc. HCl (HBr or H_2SO_4) at 100° (bath) (not in the cold) gives, after esterification (CH_2N_2) and chromatographic purification (Al_2O_3), coproglauco bilin II β Me₄ ester [1':8'-dihydroxy-1:4:5:8-tetramethyl-2:3:6:7-tetra-(β -carboxymethoxyethyl)bilin] (A, R = $[\text{CH}_2]_2\cdot\text{CO}_2\text{Me}$), m.p. 201° , which has the properties of glauco bilin IX α .



(A.)

5-Bromo-5'-methoxy-4:4'-dimethyl-3:3'-diethylpyrromethene (II) (Zn salt, m.p. 218°), 40% CH_2O ,

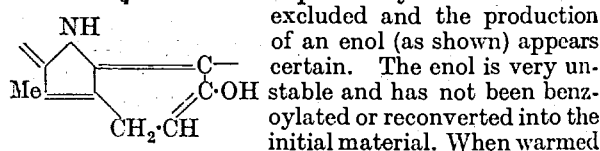
and conc. HCl at 100° afford *isoetioglucobilin* [1': 8'-*dihydroxy*-1 : 4 : 5 : 8-*tetramethyl*-2 : 3 : 6 : 7-*tetraethylbilin*] (*A*, R = Et), sinters at 283° (? 183°), which resembles natural glucobilin. Various unsuccessful attempts to replace the Br of (I) by other groups are noted. Reduction of (I) with Pd-CaCO₃ and N₂H₄·H₂O in boiling dil. MeOH-KOH, esterification (MeOH-HCl), and chromatographic purification (Al₂O₃) gives 5-methoxy-4 : 4'-dimethyl-3 : 3'-di-(β-carbomethoxyethyl)pyrromethene, m.p. 157° (5-p-sulphobenzenazo-derivative hydrochloride, m.p. 174°). With Pd-CaCO₃ and boiling dil. MeOH-KOH, (I) affords (after esterification) 1' : 8'-dimethoxy-1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetra-(β-carbomethoxyethyl)dipyrromethene (B, R =

[CH₂]₂-CO₂Me), m.p. 184°. Similarly, (II) yields 5-methoxy-4 : 4'-dimethyl-3 : 3'-diethylpyrromethene [which with PhN₃Cl in MeOH-CHCl₃ gives 5-benzenazo-5'-hydroxy-4 : 4'-dimethyl-3 : 3'-diethylpyrromethene (hydrochloride, m.p. 143°)] or 1' : 8'-dimethoxy-1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetraethyldipyrromethene (B, R = Et), m.p. 247°. 5 : 5'-Dibromo-4 : 4'-dimethyl-3 : 3'-di-(β-carbomethoxyethyl)pyrromethene and Pd-CaCO₃ in boiling MeOH afford the Pd salt (III), m.p. 168°, of 1' : 8'-dibromo-1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetra-(β-carbomethoxyethyl)dipyrromethene (IV), m.p. 225°; (III) is separated from unchanged material and by-products by adsorption on Al₂O₃ and is converted into (IV) by 48% HBr-COMe₂. With HI-COMe₂, (III) yields the 1' : 8'-I₂-derivative, m.p. 237°. 1' : 8'-Dichloro-1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetra-(β-carbomethoxyethyl)dipyrromethene, m.p. 241°, obtained from the Pd salt of the Et₃ ester [corresponding with (IV)] and conc. HCl in COMe₂ or EtOH, undergoes reductive fission with Zn dust and AcOH to 5'-chloro-4 : 4'-dimethyl-3 : 3'-di-(β-carbomethoxyethyl)pyrromethene, m.p. 147°. 5 : 5'-Dibromo-4 : 4'-dimethyl-3 : 3'-diethylpyrromethene and Pd-CaCO₃ in boiling EtOH yield a Pd salt, C₃₀H₃₄N₄Br₂Pd, m.p. >320°, converted by COMe₂-conc. HCl into 1' : 8'-dichloro-1 : 4 : 5 : 8-tetramethyl-2 : 3 : 6 : 7-tetraethyldipyrromethene, m.p. 291°.

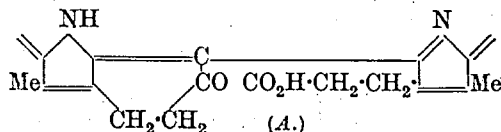
H. B.

Chlorophyll. LXXXV. Constitution of the verdins and synthetic rhodins. H. FISCHER and C. G. SCHRÖDER (Annalen, 1939, 537, 250-286).—The product obtained by the action of boiling AcOH on mesorhodin ester (Fischer et al., A., 1936, 1128) is separated into mesoverdin ester I (complex Cu salt) and an isomeride, m.p. 228°. 2 : 3 : 5 : 8-Tetramethyl-1 : 4-dipropylporphin-6 : 7-dipropionic acid is transformed by conc. H₂SO₄ + oleum into 2 : 3 : 5 : 8-tetramethyl-1 : 4-dipropyl-7-γ-propanoneporphin-6-propionic acid (propylrhodin), converted by CH₂N₂ in Et₂O into the Me ester, m.p. 262° (Cu complex salt and its oxime which gives the Cu-free oxime identical spectroscopically with mesorhodinoxime); these appear to be homogeneous. Whereas the rhodins are easily isomerised to the verdins the Cu complex salts show much greater stability. Thus mesorhodin ester Cu salt is unchanged when boiled for 30 hr. with glacial AcOH but is transformed by succinic acid at 250° into mesoporphyrin, identified

as the Me ester, m.p. 206°. Mesorhodin ester Zn complex salt is converted by NaOEt in EtOH followed by 12% HCl into a porphyrin, C₃₅H₃₈O₃N₄, m.p. 232°, spectroscopically very similar to mesoporphyrin and apparently isomeric with mesorhodin. The same result is obtained in O₂ or N₂ or after addition of KMnO₄ so that the possibility of oxidation is



excluded and the production of an enol (as shown) appears certain. The enol is very unstable and has not been benzoylated or reconverted into the initial material. When warmed with AcOH or treated with mineral acid it is converted into a green pigment with high acid val. and non-characteristic spectrum. Similarly the Zn complex salt of propylrhodin is converted into the cryst. enol, C₃₇H₄₂O₃N₄, m.p. 224° (Cu complex salt, decomp. 250°). Under similar conditions the Zn complex salt of phyloerythrin is oxidised to completely decomposed pigment and chloroporphyrin e₅-lactone. The formation of verdin from rhodin by means of boiling AcOH is invariably accompanied by the destruction of a large proportion of the pigment. This can be considerably avoided by replacing AcOH by HCl-C₅H₅N or NH₂Ph.HCl-C₅H₅N, or best by use of NH₂CO-NH-NH₂.HCl. In every case there is formed a brown intermediate phase which requires the presence of an oxidising agent for its transformation into the final green stage. The conversion of rhodin into verdin is not an isomerisation but a dehydrogenation. Mesoverdin is therefore *A*. Ver-



din VII (I) is oxidised by KMnO₄ in ice-cold C₅H₅N to dihydroxyrhodin VII, m.p. 269° (dibenzoate, m.p. 263°, and its Cu compound). Analogously propylverdine (II) is oxidised to 12 : 13-dihydroxypropylrhodin (III) m.p. 196° (unstable, complex Cu salt), with some "propylphyloerythrin diketone," m.p. 256°, spectroscopically identical with phyloerythrin diketone. Conc. H₂SO₄ converts (III) into a green pigment which gives a Bz derivative whilst alkaline KMnO₄ transforms it into "propylchloroporphyrin e₅ monoester lactone." (II) in C₅H₅N is transformed by OsO₄ in Et₂O into 9 : 10-dihydroxypropylrhodin, m.p. 198°, and some propyl-e₅ lactone. CHN₂-CO₂Et and (I) give a green pigment. Attempts to hydrogenate mesoverdin and rhodin are described. Pyrro-rhodin is transformed by boiling C₅H₅N-AcOH into pyrroverdin, C₃₁H₄₀ON₄ (oxime; Cu complex salt and its oxime). KMnO₄ in COMe₂ oxidises (II) to propylrhodoporphyrin-γ-carboxylic anhydride, m.p. 274°, converted by C₅H₅N-MeOH-CH₂N₂ in Et₂O into a compound spectroscopically identical with rhodoporphyrin-γ-carboxylic acid from chlorophyll and degraded by HI to "propylrhodoporphyrin," C₃₆H₄₂O₄N₄, m.p. 185°. Oxidation of mesoverdin I with KMnO₄ yields a compound, m.p. 248°. H. W.

Hæmocuprein and hepatocuprein, copper-protein compounds of blood and liver, respec-

tively, in mammals. T. MANN and D. KEILIN (Proc. Roy. Soc., 1938, B, 126, 303—315).—Partly a more detailed account of work previously reviewed (A., 1938, II, 423). Haemocuprein (I) is also isolable (impure) from red blood corpuscles of man, sheep, and horse. The total Cu of blood is probably present as (I). Irreversible reduction (loss of colour) of (I) occurs with $\text{Na}_2\text{S}_2\text{O}_4$. The almost colourless *hepatocuprein* (II) (0.34% Cu) is isolated from ox liver by a method similar to that used for (I). Dil. $\text{CCl}_3\cdot\text{CO}_2\text{H}$ readily removes Cu from (I) and (II), which are probably albumins, do not combine with mol. O_2 , and do not catalyse directly any of the reactions catalysed by polyphenol or cytochrome oxidases, peroxidase, catalase, or carbonic anhydrase. The possible significance of (I) and (II) in relation to the effects of Cu on blood formation, growth, and metabolism of organisms is discussed. H. B.

3-Acylisooxazole compounds. II. T. AJELLO and S. CUSMANO (Gazzetta, 1938, 68, 792—802; cf. A., 1938, II, 162).—3-Acetyl-5-phenylisooxazole (I) with $\text{NH}_2\text{OH}\cdot\text{HCl}$ gives the oxime (II), m.p. 170° (Bz derivative, m.p. 159°), hydrolysed by boiling 10% HCl . Boiled with free NH_2OH , (I) forms the oxime (III), m.p. 105°, of 3-methyl-4-phenacyl-1:2:5-oxadiazole (*semicarbazone*, m.p. 190—192°), to which it is hydrolysed by boiling 25% H_2SO_4 . Similarly (II) with NH_2OH gives (III). 3-Benzoyl-5-methylisooxazole (IV) with $\text{NH}_2\text{OH}\cdot\text{HCl}$ gives the oxime (V), m.p. 110° (Bz derivative, m.p. 101°), of 3-phenyl-4-acetonyl-1:2:5-oxadiazole, m.p. 93° (p-nitrophenylhydrazones, m.p. 158—160°; *semicarbazone*, m.p. 187°), and the oxime (VI), m.p. 133° (Bz derivative, m.p. 118—121°), of (IV), to which (VI) is hydrolysed by dil. H_2SO_4 . With NH_2OH , (VI) gives some (V).

E. W. W.

Heterocyclic compounds containing nitrogen.
XL. Condensation of o-nitrobenzaldehyde with phenylnitromethane. P. RUGGLI and B. HEGEDÜS. **XLI. Additive products of isatogen.** P. RUGGLI, B. HEGEDÜS, and E. CASPAR (Helv. Chim. Acta, 1939, 22, 405—410, 411—415; cf. Baker *et al.*, A., 1927, 550; 1939, II, 178).—XL. $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{CH}_2\text{Ph}\cdot\text{NO}_2$ in EtOH , with $\text{NH}_2\text{Me}\cdot\text{EtOH}$, give *o*- α -dinitrostilbene (I) ($\text{Zn}\cdot\text{AcOH}$ at 60—90° gives 2-phenylindole) and *o*-nitrobenzoylbenzoylphenylmethaneoxime (II), m.p. 164° [α -oximino- γ -keto- $\alpha\beta$ -diphenyl- γ -*o*-nitrophenylpropane] (cf. Worrall, A., 1936, 213). Its mode of formation, through an additive product of (I) and $\text{CHPh}_2\cdot\text{NO}_2$, is discussed. (II) and $\text{KOH}\cdot\text{MeOH}$ at 100° (bath) give (enol form loses H_2O) 3:4-diphenyl-5-(*o*-nitrophenyl)isooxazole, m.p. 127° (also formed by aq. alkalis or by boiling AcOH or mineral acids), reduced by H_2 (Raney Ni) in AcOH at room temp. to the corresponding amine, m.p. 185° (*Ac* derivative, m.p. 192°), also obtained from (II) and $\text{Zn}\cdot\text{AcOH}$. Catalytic hydrogenation (as above) of (II) (+8 H) at 70° gives a compound, $\text{C}_{21}\text{H}_{15}$ or 17ON , m.p. 222° (not 4-keto-2:3-diphenylquinoline).

XLI. 2-Phenylistatogen (III) or its 6- CO_2Et -derivative, with MgPhBr in dioxan- Et_2O , adds $\text{Ph}\cdot\text{H}$, giving 1-hydroxy-3-keto-2:2-diphenylindoline, m.p. 240°, and its 6-carbethoxy-derivative (*dihydroindole*), m.p. 207°, respectively. (I) and Ac_2O at 100° (bath)

for 14 hr. give an adduct, 3-keto-1:2-diacetoxy-2-phenylindoline, m.p. $\sim 184^\circ$ with previous reddening and decomp., or m.p. 185° (rapid heating); (I) and $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$ at 50° give 1:3:5-triacetoxy-2-phenylindole, m.p. 194—195°. A. T. P.

Cyanines.—See B., 1939, 440.

Benzthiazole derivatives. I. Reactivity of the methylthiol group in quaternary salts of 1-methylthiobenzthiazole. W. A. SEXTON. II. Conversion of 1-alkylthiobenzthiazoles into 1-thio-2-alkyl-1:2-dihydrobenzthiazoles. F. P. REED, A. ROBERTSON, and W. A. SEXTON (J.C.S., 1939, 470—473, 473—476).—I. The methosulphate of 1-methylthiobenzthiazole (I) with aq. NaOH gives 2-methylbenzthiazolone and with aq. Na_2S affords 1-thio-2-methyl-1:2-dihydrobenzthiazole. The following compounds have been obtained from derivatives substituted in the C_6H_4 ring: 4-chloro-2-methylbenzthiazolone, m.p. 109—110°; 4-chloro-1-thio-2-methyl-1:2-dihydrobenzthiazole, m.p. 169°; 1-methylthiol-4-methylbenzthiazole, m.p. 52—54°; 2:4-dimethylbenzthiazolone, m.p. 121°; and 1-thio-2:4-dimethyl-1:2-dihydrobenzthiazole, m.p. 190°. In the action of EtI on (I) a quaternary salt is formed in which the alkyls have been interchanged. 1- β -Hydroxyethylthiobenzthiazole, m.p. 56—58°, is changed on heating into 1-hydroxybenzthiazole.

II. When heated with a trace of I, (I) is transformed into 1-thio-2-methyl-1:2-dihydrobenzthiazole. This reaction may be applied to the prep. of the following: 1-thio-2-n-propyl-, m.p. 74°, -2-isoamyl-, m.p. 54—55°, -2- α -methylallyl-, m.p. 115°, and -5-methoxy-2-methyl-1:2-dihydrobenzthiazole, m.p. 87°, and 5-chloro-1-thio-2-methyl-1:2-dihydrobenzthiazole, m.p. 130°. Sodio-1-thiobenzthiazole and CH_2PhCl give 1-benzylthiobenzthiazole, converted into 1-thio-2-benzyl-1:2-dihydrobenzthiazole, m.p. 149°, also obtained from (I) and CH_2PhCl . 2-Benzylthiol- β -naphthathiazole, m.p. 85—86°, is not isomerised but yields 2-thiol- β -naphthathiazole. 4-Chloro-1-benzylthiobenzthiazole, m.p. 73—75°, is transformed into 4-chloro-1-thio-2-benzyl-1:2-dihydrobenzthiazole, m.p. 184—185°. F. R. S.

α -Amino- β -(4-methylthiazole-5)-propionic acid, a possible precursor of aneurin. C. R. HARRINGTON and R. C. G. MOGGIDGE (J.C.S., 1939, 443—446).—The presence of a hydroxyethyl side-chain in the thiazole component of the aneurin mol. suggests the possible biological formation of this compound from the corresponding α -aminopropionic acid; a further extension of this idea brings the aneurin thiazole into hypothetical relationship with the known natural product methionine. *Et* 4-methylthiazole-5-carboxylate hydrochloride, m.p. 155°, with aq. NH_3 gives 4-methylthiazole-5-carboxylamide, m.p. 149°, dehydrated to 5-cyano-4-methylthiazole, b.p. 86—88°/14 mm., m.p. 33.5° [hydrochloride, m.p. 145° (decomp.)]. The nitrile and $\text{HCl}\cdot\text{SnCl}_2$ form 4-methylthiazole-5-aldehyde, m.p. 72.5° (phenylhydrazones, m.p. 161°; *semicarbazone*, m.p. 241°), which through the azlactone, m.p. 199°, is converted into α -amino- β -(4-methylthiazole-5)-propionic acid, m.p. 240° (decomp.) [dipicrate, m.p. 146° (decomp.)],

forming with NHPH_2 β -(4-methylthiazole-5)-ethylamine dihydrochloride, m.p. 246°. F. R. S.

2-Ethylbenzthiazolydenepentamethene - ω -aldehyde and the benzselenazolydene analogue.—See B., 1939, 357.

Carbazoles, diphenylene oxides, and benzthiazoles.—See B., 1939, 442.

Alkaloids of *Senecio* species. III. *Senecio integerrimus*, *S. longilobus*, *S. spartioides*, and *S. ridellii*. IV. *Erechtites hieracifolia* (L.), Raf. R. H. F. MANSKE (Canad. J. Res., 1939, 17, B, 1—7, 8—9).—III. The main alkaloid in *S. integerrimus* is senecionine (I), but it also contains a small quantity of an alkaloid *integerrimine*, $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}$, m.p. 172—172.5°, $[\alpha]_D^{25} + 4.3^\circ$ in MeOH, hydrolysed by NaOH-EtOH to retronecine (II) and *integerrinecic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_5$, m.p. 151°. *S. longilobus* contains *longilobine*, $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}$, m.p. 217—218°, $[\alpha]_D^{25} - 79.2^\circ$ in 95% EtOH (*methiodide*, m.p. 249°), hydrolysed to (II) and *longinecic acid*, $\text{C}_{10}\text{H}_{14}\text{O}_5$, m.p. 126°. *S. spartioides* yields *seneciophylline* and a small quantity of *spartioidine*, $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}$, m.p. 178°. *S. ridellii* contains *ridelline*, $\text{C}_{18}\text{H}_{25}\text{O}_6\text{N}$, m.p. 196° (*methiodide*, m.p. 259°), and *S. pseudoarnica* contains (I).

IV. *E. hieracifolia* yields to MeOH *hieracifoline*, $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}$, m.p. 227°, $[\alpha]_D^{25} - 89.7^\circ$ in CHCl_3 , hydrolysed by MeOH-KOH to retronecine and *hieracinecic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_5$, m.p. 132°, and an alkaloid, m.p. 237°, which is also of the *Senecio* species. J. D. R.

Sulphanilamide additive compounds with cinchona alkaloids. E. H. STUART, H. M. POWELL, C. L. ROSE, and F. E. BIBBINS (J. Amer. Pharm. Assoc., 1939, 28, 90—95).—Additive compounds of sulphanilamide were prepared (vals. in parenthesis are for $[\alpha]_D^{25}$ in H_2O) with: *quinine*, 2HCl , H_2O , m.p. 110°, (−150°); *quinine*, 2HCl , m.p. 130°, (−155°); *quinine*, 3HCl , m.p. 150°, (−144°); *quinine*, 2HBr , m.p. 211°, (−126°); *quinine*, 2HI , m.p. approx. 70°, (−92.5°); *quinine*, H_2SO_4 , m.p. 208°, (−147°); *quinine*, $1.5\text{H}_2\text{SO}_4$, m.p. 186°, (−112°); *quinine sulphamic acid*, m.p. 133°, (−131°); *quinine sulphanilysulphanilic acid*, m.p. 153°; *quinidine*, 2HCl , m.p. approx. 135°, (+170°); *quinidine*, 2HBr , m.p. approx. 130°, (+137.5°); *quinidine*, H_2SO_4 , m.p. 172°, (+164°); *quinidine*, $1.5\text{H}_2\text{SO}_4$, m.p. 125°, (+152°); *euquinine*, 2HCl , m.p. approx. 135°, (−55°); *euquinine*, 2HBr , m.p. approx. 135°, (−43°); *euquinine*, H_2SO_4 , m.p. 91°, (−51.5°); *cinchonine*, 2HCl , m.p. approx. 135°, (+132°); *cinchonine*, 2HBr , m.p. approx. 130°, (+112°); *cinchonine*, H_2SO_4 , m.p. approx. 120°, (+123.5°); *cinchonidine*, 2HCl , m.p. approx. 136°, (−93.7°); *cinchonidine*, 2HBr , m.p. approx. 135°, (−78°); *cinchonidine*, H_2SO_4 , m.p. 180°, (−92.5°); the following additive compounds with quinine were also prepared: 4:4-diaminodiphenylsulphone, H_2SO_4 , m.p. 176°; *disulphanilamide*, 2HCl , m.p. 115°; *disulphanilamide*, H_2SO_4 , m.p. 207°, (−145°); *N-hydroxysulphanilamide*, H_2SO_4 , m.p. 187°; *p-benzylaminobenzenesulphonamide*, H_2SO_4 , m.p. 104°; *p-mandylaminobenzenesulphonamide*, H_2SO_4 , m.p. 190°; 2-(*p*-aminobenzenesulphonamido)pyridine, H_2SO_4 , m.p. 139°. All m.p. corr. Several of the above compounds show thera-

peutic activity in experimental hæmolytic streptococcal infections but none is active against staphylococcal infections or human influenza virus infections in mice; those tested in malaria-infected canaries are active only in proportion to their alkaloid content.

F. O. H.

Strychnos alkaloids. CIII. Behaviour of the methobromide of the Hanssen acid $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2$ during hydrogenation and treatment with bromine. H. LEUCHS and H. L. LOUIS (Ber., 1939, 72, [B], 490—494).—Brucine in CHCl_3 is treated with Me_2SO_4 and the product is acted on by 14.5N- HNO_3 . The quinone is oxidised with Br and the product is separated as far as possible as the compound (I), $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\text{MeBr}$, the residue being isolated as the *methoperchlorate* (II). (I) absorbs 2 H_2 (PtO_2 in H_2O) and yields the *perchlorate* (III), $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\text{MeClO}_4$, $[\alpha]_D^{25} + 6.9^\circ$ in 0.1N-NaOH. The methiodide of the Me_2 ester similarly gives the compound, $\text{C}_{21}\text{H}_{20}\text{O}_6\text{N}_2\text{MeI}$. With Na-Hg in H_2O (I) yields the substance, $\text{C}_{19}\text{H}_{24}\text{O}_6\text{N}_2\text{MeClO}_4$, (corresponding *bromide*, $[\alpha]_D^{25} 17.3^\circ$ in H_2O). Methylation (Me_2SO_4) of the Hanssen acid followed by treatment with 8N-HBr leads to the compound, $\text{C}_{19}\text{H}_{24}\text{O}_7\text{N}_2\text{MeBr}$, dehydrated by boiling N-HClO_4 to the substance, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\text{MeClO}_4$, hydrogenated (PtO_2) to the compound, $\text{C}_{19}\text{H}_{28}\text{O}_7\text{N}_2\text{MeClO}_4$, and oxidised by Br to the *methobromide* (IV), $\text{C}_{19}\text{H}_{28}\text{O}_7\text{N}_2\text{BrMeBr}$. Br- H_2O oxidises (I) to (IV) [corresponding *methoperchlorate*], hydrogenated to the substance, $\text{C}_{19}\text{H}_{28}\text{O}_7\text{N}_2\text{MeClO}_4$, and converted by aq. Ba(OH)_2 into the compound, $\text{C}_{19}\text{H}_{26}\text{O}_6\text{N}_2\text{BrMeClO}_4$. (II) and Br- H_2O give the substance, $\text{C}_{19}\text{H}_{21}\text{O}_6\text{N}_2\text{BrMeClO}_4$, m.p. > 300° after becoming brown at 230°, hydrogenated (PtO_2 in H_2O) to (III). The methobromide of the dehydro-Hanssen acid is converted by Br- H_2O into the *methobromide*, $\text{C}_{19}\text{H}_{25}\text{O}_7\text{N}_2\text{BrMeBr}$. H. W.

Strychnos alkaloids. CIV. Quinones from ψ - or 9-monohydroxy-brucine and an unusual isomerisation of the nitroquinone. H. LEUCHS and H. SEEGER (Ber., 1939, 72, [B], 495—499).— ψ -Brucine (I) is oxidised by 5N- HNO_3 at −10° to the *o*-quinone, $\text{C}_{21}\text{H}_{20}\text{O}_5\text{N}_2$ (*picrate*), converted by SO_2 into the quinol, $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2$ (*perchlorate*). (I) is transformed by 5N- HNO_3 at 45—60° into the nitroquinone hydrate (II), $\text{C}_{21}\text{H}_{21}\text{O}_8\text{N}_3$ [*perchlorate* (II)], which is reduced by H_2SO_3 to the nitro-*o*-quinol hydrate, $\text{C}_{21}\text{H}_{23}\text{O}_8\text{N}_3$ (*perchlorate*), and by Sn-12N-HCl at 20—60° to the amino-*o*-quinol hydrate (*diperchlorate*; *dihydrochloride*). Catalytic hydrogenation (PtO_2 in H_2O) of (III) affords the compound, $\text{C}_{21}\text{H}_{25}\text{O}_5\text{N}_3$, 2HClO_4 . Hot H_2O isomerises a yellow salt of (II) to the red hydrate, $\text{C}_{21}\text{H}_{21}\text{O}_8\text{N}_2$, m.p. > 300°, which is sol. in alkali or alkali H carbonate but does not appear to form salts with acids. NH_2OH salts and (III) at 40—50° give the *nitroquinoneoxime*, $\text{C}_{21}\text{H}_{22}\text{O}_8\text{N}_4$ (*perchlorate*), the *hydrochloride* of which it reduced (PtO_2 in 0.04N-HCl) to diaminohydroxydihydro- ψ -strychnine, isolated as the triperchlorate. The perchlorate of the *nitroquinonesemicarbazone* is described. H. W.

6-Benzoylmorphine. C. MANNICH and G. STEWERT (Arch. Pharm., 1939, 277, 128—130).—Morphine 3- CH_2Ph ether with BzCl in $\text{C}_5\text{H}_5\text{N}$ at room

temp. (3 days) gives the 6-benzoate hydrochloride, m.p. 130—135°, hydrolysed by 38% HCl at room temp. to 6-benzoylmorphine, m.p. 269—270° (decomp.) [hydrochloride, m.p. 241—243° (decomp.); *H* tartrate, $+5\text{H}_2\text{O}$, m.p. ~ 136 —138°, decomp. 170—172°], which is analgesic but rather toxic. R. S. C.

Alkaloid in bulbs of *Narcissus tazetta*, L. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1939, 15, 128—132).—Extraction of the bulbs with EtOH yields *suisenine* (I), $\text{C}_{17}\text{H}_{19}\text{O}_5\text{N}$, m.p. 229° (Me_1 ester, m.p. 188°; benzoate, m.p. 196°; hydrochloride, m.p. 180°; picrate, m.p. 189°; *Pt* salt, m.p. 194°). (I) contains 1 OMe, 1 OH, and 1 CH_2O_2 , but no NMe. Oxidation with alkaline KMnO_4 gives a substance, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$, m.p. 244°. (I) may contain a phenanthridine nucleus, and the absorption spectrum and reactions point to the presence of an isoquinoline nucleus. J. N. A.

Active principles of curare. P. DE BERRÉDO-CARNEIRO (Bull. Soc. Chim. biol., 1939, 21, 282—293).—Two bases, *strychnolethaline*, $\text{C}_{22}\text{H}_{27}\text{O}_5\text{N}$, and *curaethaline*, $\text{C}_{25}\text{H}_{31}\text{O}_7\text{N}$, have been isolated by means of their silicotungstates (base : silicotungstic acid = 3 : 1) from curare and from the bark of *Strychnos lethalis*. The former is pptd. at p_{H} 9.3 and the latter at p_{H} 5.0. Their fluorescence spectra show absorption max. at 559 μ . and at 466 and 557 μ . respectively. P. G. M.

Alkaloids of han-fang-chi. Fangchinoline, a demethyltetrandrine. C. K. CHUANG, C. Y. HSING, Y. S. KAO, and K. T. CHANG (Ber., 1939, 72, [B], 519—525).—Exhaustive extraction of han-fang-chi with hot EtOH leads to tetrandine (I), m.p. 216—217°, $[\alpha]_{\text{D}}^{25} +285.4^\circ$ in CHCl_3 , identical with the product isolated from *Stephanea tetrandra*, and fangchinoline (II), $\text{C}_{37}\text{H}_{40}\text{O}_6\text{N}_2$, m.p. 237—238°, $[\alpha]_{\text{D}}^{25} +255.1^\circ$ in CHCl_3 [picrate (from EtOH), m.p. 186° (decomp.); (from COMe_2), m.p. 224° (decomp.)]. (II) is insol. in alkalis, and gives a blue-green colour with FeCl_3 in EtOH and a faint Liebermann reaction. It contains 1 OH and 3 OMe. It is transformed by CH_2N_2 in $\text{MeOH-Et}_2\text{O}$ into (I). Oxidation of fangchinoline *Et ether*, m.p. 116—117° [picrate, m.p. 242° (decomp.)], with KMnO_4 affords 6-methoxy-3 : 4-dicarboxydi-phenyl ether, m.p. 302—304°, identical with that derived from (I). H. W.

Valerian; a new alkaloid. J. J. BLACKIE and D. RITCHIE (Pharm. J., 1939, 142, 299—300).—Extraction of dried valerian root with 90% EtOH followed by evaporation and extraction of the aq. solution with $\text{C}_2\text{H}_{11}\text{OH}$ yields an oily base from which no cryst. derivative could be prepared.

J. D. R.

Relative reactivities of organometallic compounds. XXI. Organolead radicals and derivatives. H. GILMAN and J. C. BAILIE. XXII. Hydrogen chloride cleavage rates of *p*-anisyl-2-furyl lead compounds. H. GILMAN and E. B. TOWNE. XXIII. Allylic rearrangements. XXIV. Reaction rates of benzoyl halides with mercury-di-*p*-tolyl. H. GILMAN and J. F. NELSON (J. Amer. Chem. Soc., 1939, 61, 731—738, 739—741, 741—743, 743—744; cf. A., 1939, II, 131).—XXI. *Pb tri-a-*

naphthyl, m.p. 268—269° (darkens at 255°), is best obtained from $1\text{-C}_{10}\text{H}_7\text{Li}$, reaction of $1\text{-C}_{10}\text{H}_7\text{MgBr}$ with PbCl_2 being unsatisfactory. MgArX and PbCl_2 give PbPh_3 , darkens at 160°, m.p. 224—225° (that of (PbPh_4) , *Pb tri-p-*, m.p. 244—255°, and *-o-tolyl*, m.p. 248—250° (decomp. 238—242°), *trimesityl*, m.p. $>325^\circ$, *tri-p-*, m.p. 198—200° (decomp.) [some $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}p)_4$ also formed], and *-o-anisyl*, m.p. 198—201° (decomp.), *tri-p-*, m.p. 178—179° (decomp.), and *-o-phenetyl*, m.p. 170—171° (decomp.). *Pb tri-m-tolyl*, m.p. 109°, is best obtained from $(m\text{-C}_6\text{H}_4\text{Me})_3\text{PbBr}$ and Na in liquid NH_3 , as the Grignard reaction gives also much $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}m)_4$; PbPh_3 is similarly obtained from PbPh_3I . PbR_3X and 2 Na in liquid NH_3 , however, give PbR_3Na . Prep. of PbEt_3 in 69% yield from PbEt_3Cl and Na in liquid NH_3 is detailed. PbR_3 , CH_2PhCl , and 2 Na in liquid NH_3 give $\text{PbPh}_3\text{CH}_2\text{Ph}$, *Pb tri-p-tolyl*, m.p. 81—82°, *tri-p-*, m.p. 76—77°, and *-o-anisyl*, m.p. 80—81°, and *tricyclohexyl-benzyl*, m.p. 228° (decomp.). *Pb tricyclohexyl*, darkens at 187°, decomp. 196°, is obtained by the Grignard reaction. Addition of PbPh_3 and 2 Na in liquid NH_3 to CHPh_2Cl in Et_2O gives 54% of *Pb triphenyl benzhydryl*, m.p. 122° (decomp. 130°). PbPh_3I is prepared in 88% yield from PbPh_4 and I in CHCl_3 . $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}m)_4$, I, and solid CO_2 in $\text{C}_5\text{H}_5\text{N}$ give 78% of *Pb tri-m-tolyl bromide*, m.p. 146—147°. Pyrolysis of PbR_3 in xylene to Pb and PrR_4 indicates the following order of decreasing thermal stability, which is obviously influenced by steric, as well as by structural, factors : mesityl, cyclohexyl, $1\text{-C}_{10}\text{H}_7 > o\text{-} > p\text{-C}_6\text{H}_4\text{OEt}$, $\text{-C}_6\text{H}_4\text{OMe}$, $\text{-C}_6\text{H}_4\text{Me} > m\text{-C}_6\text{H}_4\text{Me}$, $\text{Ph} > \text{Et}$, Me . The following are incidentally described : *Pb tetra-m-tolyl*, m.p. 122—123°, *-p-*, m.p. 145—146°, and *-o-anisyl*, m.p. 148—149°, *-p-*, m.p. 110°, and *-o-phenetyl*, m.p. 219—220°. Pyrolysis of a mixture of $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}p)_3$ and $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ gives 65% of $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}p)_4$ and 57% of $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}p)_4$. PbR_4 and $\text{Mg} + \text{MgBr}_2$ give (probably by way of PbR_3MgBr) MgRBr and PbR_2 , the PbR_2 then decomp. to PbR_4 and Pb; if, however, R is sterically hindered (*o*-anisyl, mesityl, or cyclohexyl), the product is PbR_3I . PbEt_3 and PbEt_3Br (modified prep.), but not PbEt_3Cl or SnEt_3Cl , react with Mg, giving Pb and PbEt_4 , but this does not define the mechanism of the $\text{Mg} + \text{MgBr}_2$ reaction. PbPh_3 and $\text{Pb}(\text{C}_6\text{H}_4\text{Me-}p)_3$ with MgI_2 in $\text{Et}_2\text{O-C}_6\text{H}_6$ give PbR_3I . $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ and I in cold CHCl_3 give 50.6% of PbR_4 and 7.1% of *Pb di-p-anisyl di-iodide*, m.p. 122—123° (softens at 116°); $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}o)_3$ gives 41.2% of $(o\text{-OMe-C}_6\text{H}_4)_3\text{PbI}$; $\text{Pb}(\text{C}_6\text{H}_4\text{OEt-}p)_3$ and I in $\text{C}_5\text{H}_5\text{N}$ give 45.5% of *Pb tri-p-phenetyl iodide*, m.p. 152°. PbPh_3 and HCl in CHCl_3 gives 82.6% of PbCl_2 and 16.5% of PbPh_2Cl_2 . Attempts to prepare PbHR_3 from PbR_3Na by NH_4Br in liquid NH_3 failed.

XXII. *p*-OMe- $\text{C}_6\text{H}_4\text{MgBr}$ and PbCl_2 in $\text{Et}_2\text{O-PhMe}$ give mixtures, but in Et_2O 65.4% of $\text{Pb}(\text{C}_6\text{H}_4\text{OMe})_3$ (I), m.p. 198—200° (decomp.), and 3.6% of $\text{Pb}(\text{C}_6\text{H}_4\text{OMe-}p)_4$ (II) are obtained. Pyrolysis of (I) gives $\sim 75\%$ of (II). HCl and (II) in hot CHCl_3 give 90.4% of *Pb tri-p-anisyl chloride* (III), m.p. 152—153° (decomp.), and 8.1% of *Pb di-p-anisyl dichloride* (IV), the latter product being obtained in 98.6% yield in hot C_6H_6 . With Mg 2-furyl iodide (III) gives *Pb*

tri-p-anisyl 2-furyl, m.p. 83°, and (IV) gives 55.9% of *Pb di-p-anisyl di-2-furyl*, m.p. 72–73°. Cleavage of these mixed compounds by HCl proceeds with fission of the furyl, showing that 2-furyl is the nucleus most readily lost from Pb. *p*-OMe-C₆H₄Li and (III) give *Pb triphenyl p-anisyl*, m.p. 152°, which with HCl-CHCl₃ gives PbPh₂Cl₂ (37.5%), PbPh₃Cl (60.7%), and PhOMe (46.3%). Pb(C₆H₄-OMe-*p*)₃ and HCl-CHCl₃ give, according to the conditions, PbR₃Cl or PbR₂Cl₂; *Pb di-p-anisyl diacetate* is described.

XXIII. Allylic rearrangements occur when metal-benzyl compounds of Zn, Cd, Hg, or Al react with CH₂O, AcCl, or CO₂, the amount of rearrangement increasing with increasing reactivity of the compound.

XXIV. The relative reactivities, BzI > BzBr > BzCl > BzF, with Hg(C₆H₄Me-*p*)₂ are established by comparing the halides in pairs. It follows that reaction of RCOHal with HgR₂ does not occur by way of an additive compound. R. S. C.

Aryl selenohalides. VI. Diphenylselenohalides and a new method of formation of diphenylene selenide. O. BEHAGEL and K. HOFMANN (Ber., 1939, 72, [B], 582–593; cf. A., 1935, 1257).—Addition of KSeCN to a diazotised solution of 2-aminodiphenyl hydrochloride gives 2-selenocyanodiphenyl, b.p. 200–202°/15 mm., converted by NH₃ in boiling EtOH into 2:2'-didiphenyl diselenide, m.p. 77–78°. This is transformed by a small excess of Br in CHCl₃ into *Se 2-diphenyl tribromide* (I), m.p. 128°, and by Cl₂ in CHCl₃ into the trichloride (II), m.p. 140–150° (decomp.). Hydrolysis of (I) or (II) with dil. aq. Na₂CO₃ gives 2-diphenylseleninic acid, m.p. 128°. Addition of (I) or (II) to 25% KOH-MeOH yields diphenylene selenide (III), m.p. 78–79°. Interaction of PhSeH with *o*-C₆H₄Cl-NO₂ gives 2-nitrodiphenyl selenide, m.p. 91°, reduced by SnCl₂ and HCl to 2-aminodiphenyl selenide, b.p. 209–211°/15 mm., which gradually darkens on exposure to air, and is converted by diazotisation and treatment with Cu-bronze into (III). When heated in a solvent (II) loses HCl and gives diphenylene selenide dichloride, m.p. 136–137°, whereas when heated alone it affords 3-chlorodiphenylene selenide dibromide, m.p. 130–131°. (I) loses HBr vigorously at 140°, giving 3-bromodiphenylene selenide, m.p. 95–96°. A diazotised solution of 4-aminodiphenyl hydrochloride and KSeCN yield a N₂ compound which is moderately stable at room temp. but readily evolves N₂ at 80° giving 4-selenocyanodiphenyl, m.p. 94°. This is transformed by boiling NH₃-EtOH into 4:4'-didiphenyl diselenide, m.p. 184°, which is converted by Cl in CHCl₃ into the very unstable *Se 4-diphenyl trichloride* (IV), m.p. 162–164°, transformed by the requisite amount of COMe₂ in CHCl₃ into *Se 4-diphenyl monochloride*, m.p. 120–122°. *Se 4-diphenyl tribromide* (V), m.p. 126°, which readily evolves Br on exposure to air, is converted similarly into the monobromide, m.p. 165–166°. Either trihalide is converted by hot 4N-Na₂CO₃ into 4-diphenylseleninic acid, m.p. 165°. When heated in an oil-bath (IV) melts at 165° and immediately decomposes into Se₂Cl₂ and *p*-C₆H₄PhCl. When treated similarly (V) yields Se₂Br₂, SeBr₄, and *p*-C₆H₄PhBr, m.p. 87°. *o*-C₆H₄Et-NH₂ is converted into *o*-selenocynoethylbenzene, which with Br in CHCl₃

affords *Se o-ethylphenyl tribromide*, m.p. 118–121°, which passes into the monobromide when heated, is transformed by trituration with COMe₂ into 2:2'-diethylphenyl diselenide, and is hydrolysed to 2-ethylphenylseleninic acid, m.p. 124°. H. W.

Amino-acid composition of the keratins. Composition of gorgonin, spongin, turtle scutes, and other keratins. R. J. BLOCK and (Miss) D. BOLLING (J. Biol. Chem., 1939, 127, 685–693).—The indigestible (enzymes) portions of gorgonin from *Gorgonia flabellum* and *Plexaurella dichotoma*, spongin, turtle scutes, and the horny excrescence on the bill of the male *Pelicanus erythrorhyncus* (% N and S given) yield histidine 0.9, 0.1, 0.2, 1.8, and 0.9, lysine 3.3, 2.8, 3.0, 1.8, and 3.4, arginine 4.5, 4.9, 4.3, 4.2, and 5.7, cystine 9.0, 7.6, 2.8, 8.6, and 4.0, tyrosine 13.0, 13.5, 0.8, 13.1, and 5.7, tryptophan 0, 0, 0, 2.3, and 0.9, phenylalanine 5.7, 6.5, 3.3, 5.2, and 4.3, glycine 15.5, 13.7, 14.4, —, —, and diiodotyrosine +, +, +, 4.7, and —%, respectively. The mol. ratios, lysine : arginine, are 4 : 6, 4 : 6, 4 : 6, 3 : 6, and 4 : 6, respectively, and these products are thus ψ -keratins. The origin and biological relationship of eu- and ψ -keratins are discussed. R. S. C.

Physico-chemical investigations with methylated glutin. J. MATULA (Biochem. Z., 1939, 300, 284–291).—Treatment of an ethereal suspension of salt-free, dried gelatin with CH₂N₂ yields methylated glutin. The conductivity of a 0.9% solution in H₂O is 9.7×10^{-5} mho and the p_H is 7.24. The acid-binding capacity of the methylated glutin is 8.9×10^{-4} mol. per g., which corresponds with that of normal glutin. η of a solution in HCl increases to a max. of 1.332 with increasing [HCl] (up to 0.0075N-HCl) and then decreases with further increase in HCl. In every case η decreases with time, finally reaching a const. val. owing to hydrolysis of the ester. The high η and capacity to gel of glutin are not recovered. Methylated glutin has practically no base-binding capacity, and it is hydrolysed extremely easily even by very dil. NaOH. J. N. A.

Thermolysis of glutin. W. SIMON (Kolloid-Z., 1939, 86, 371–372).—The increased acid-binding capacity of gelatin caused by heating its aq. solution is not necessarily due to hydrolysis, but may arise from disaggregation leading to exposure of previously inaccessible basic groups. F. L. U.

Electrophoretic investigation of casein.—See A., 1939, III, 540.

Action of ultra-violet light on proteins. I. Indole ring. G. FLORENCE, A. DRILHON, and W. DIEN-SIANG (Bull. Soc. Chim. biol., 1939, 21, 298–318).—The effect of ultra-violet light on indole, tryptophan, and their derivatives varies considerably according to the p_H of the solution; it is more marked, as shown by absorption spectra, in NH₂-derivatives. P. G. M.

Structure of proteins. M. L. HUGGINS (J. Amer. Chem. Soc., 1939, 61, 755).—On Wrinch's cyclol theory [involving >C(OH)·N< groups] the H of the CH is only 0.67 Å. from the neighbouring C; this impossibly short distance is avoided if the cage

structure contains O·H linkings [$>\text{CO}\cdots\text{HN}<$] in place of C·N linkings. R. S. C.

Simplified combustion pipette.—See A., 1939, I, 281.

Centigram method of determining carbon and nitrogen in organic compounds. E. SUCHARDA and C. TROSKIEWICZÓWNA (Rocz. Chem., 1938, 18, 784—797).—The material is oxidised with MnO_2 in H_2SO_4 in a stream of O_2 , and the reaction gases are passed successively through H_2SO_4 , layers of heated pumice-CuO and $-\text{PbCrO}_4$, CaCl_2 , and a weighed soda-lime tube, the increase in wt. of which is determined. The N content of NH_2 -, NH -, and CN -compounds is determined by Kjeldahl distillation of the residual H_2SO_4 solution. Azo- and NO_2 -compounds are reduced with Fe in H_3PO_4 before combustion.

R. T.

Protein metabolism. II. Determination of nitrogen isotopes in organic compounds. D. RITTENBERG, A. S. KESTON, F. ROSEBURY, and R. SCHÖNHIMER (J. Biol. Chem., 1939, 127, 291—299).—N in the compound (containing 0.5—2.0 mg. N) is converted into NH_3 by a micro-Kjeldahl process and then into N_2 by treatment with NaOBr . The N_2 is analysed in a mass spectrometer, which gives the % of ^{15}N present with an accuracy of about 1%. The technique employed is described in detail.

W. O. K.

Volumetric determination of sulphur by Carius' method.—See A., 1939, I, 276.

Determination of the nitro-group. L. E. HINKEL, E. E. AYLING, and T. M. WALTERS (J.C.S., 1939, 403—406).—Limpricht's method (Ber., 1878, 11, 35) and subsequent modifications are examined. From a consideration of the sources of error the following procedure is suggested. The NO_2 -compound (I) (0.1—0.2 g.) and, if necessary, 5—6 c.c. of EtOH (aldehyde-free) are introduced into a reaction flask (air displaced by CO_2); after dissolution of the (I) 10 c.c. of H_2SO_4 (1 : 1) are added, followed by 10 c.c. of SnCl_2 [283 g. of A.R. SnCl_2 in 300 c.c. of HCl (d 1.16) made up to 1 l. with H_2O (saturated with CO_2)]. The mixture is heated to 100° in CO_2 (2 bubbles per sec.). If the substance is insol. and volatile, the condenser is washed down with 2-c.c. portions of EtOH at 30 min. intervals. After 1.5 hr. the mixture is cooled, diluted with 200 c.c. of H_2O (saturated with CO_2) and titrated with 0.6N-I. A blank is carried out.

S. H. H.

Micro-determination of alkoxyl groups. A. FLEK (Ind. Eng. Chem. [Anal.], 1939, 11, 174—177).—A modified and improved apparatus and procedure effect better dissolution of the substance, more gradual and longer heating, and thorough absorption, which are equally applicable to the analysis of liquids, semi-solids, and solids, irrespective of the no. of alkoxyl groups. Recorded analyses of 33 substances containing OMe show the accuracy to be $>$ that given by conventional procedure.

F. N. W.

Detection of carbon disulphide. A. CASTIGLIONI (Z. anal. Chem., 1939, 115, 257—259).—The yellowish-white ppt. formed with piperazine (I) is used to detect CS_2 in C_6H_6 , PhMe, xylene, COMe_2 , decal and N (A., II.)

tetra-hydronaphthalene. 2 or 3 drops of a 2% solution of (I) in 95% EtOH added to 1 c.c. of the liquid to be tested will detect 0.5 mg. of CS_2 . The reaction serves also for the detection of CS_2 in presence of thiophen or H_2S .

L. S. T.

Apparatus for the determination of acetone, acetaldehyde, β -hydroxybutyric and lactic acid, total or residual nitrogen, urea, amino-acid nitrogen, and ammonia.—See A., 1939, III, 540.

Selective oxidation of fructose with potassium ferricyanide. D. T. ENGLIS and H. C. BECKER (Ind. Eng. Chem. [Anal.], 1939, 11, 145—149).—Streptkov's method (A., 1936, 1397) of determining fructose (I) in the presence of glucose (II) by the selective oxidation of the (I) by means of alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ is not strictly accurate, as (I) has a definite reducing action, but in the presence of Na_2CO_3 (to increase the reaction rate), the rate of oxidation of (I) is unaffected by the presence of $\text{Na}_2\text{HPO}_4 \cdot 10\text{H}_2\text{O}$, whilst the oxidation of (II) is inhibited.

F. N. W.

Determination of maltose by Bertrand's method. R. KLEMEN and T. ŠKERLAK (Z. anal. Chem., 1939, 116, 169—175).—Data showing the effect of time of heating, size of containing vessel, and vol. of solution on the results obtained by Bertrand's method (A., 1907, ii, 136) are recorded. Oxidation by atm. O_2 of the Cu_2O produced from the maltose and alkaline Cu tartrate solution can introduce errors $\sim 4\%$, but these can be practically eliminated by reduction of the liquid surface to a min. Under the conditions specified, Bertrand's method gives results in agreement with the iodometric method of Willstätter *et al.* (A., 1918, ii, 337).

L. S. T.

Colorimetric determination of cysteine and cystine.—See A., 1939, III, 538.

Colorimetric determination of glutathione.—See A., 1939, III, 538.

Potentiometric titration of carotenoids with gold chloride. P. KARRER and W. JAEGER (Helv. Chim. Acta, 1939, 22, 314—322; cf. A., 1938, 11, 450).—Potentiometric titrations with AuCl_3 at $\sim 70^\circ$ in EtOH (with or without C_6H_6 or Et_2O) of α - and β -carotene, xanthophyll, lycopene, and zeaxanthin (7—8 equivs. of AuCl_3), and astacin and rhodoxanthin (2 equivs.), are recorded; crocetin, bixin, fucoxanthin, and violaxanthin are not appreciably oxidised.

A. T. P.

Identification of aromatic polynitro-compounds as addition compounds with naphthalene. O. C. DERMER and R. B. SMITH (J. Amer. Chem. Soc., 1939, 61, 748—750).—56 out of 93 aromatic polynitro-compounds give complexes with C_{10}H_8 , but some of the products are too unstable to be recrystallised and in some cases their existence is merely inferred from mixed m.p. diagrams. Compounds of C_{10}H_8 with the following are obtained: isoamyl, m.p. 46—47°, and Et 3 : 5-dinitrobenzoate, m.p. 75°; 2 : 6-dinitro-, m.p. 58—58.5°, and 3-chloro-2 : 4 : 6-trinitro-phenol, m.p. 127°; 2 : 4 : 6-trinitro-anisole, m.p. 69—70° (lit. 54°), -phenetole, m.p. 39°, and -benzaldehyde, m.p. 136.5°; 2 : 4-di-

nitro-phenetole, m.p. 41°, -anisole, m.p. 50°, -resorcinol, m.p. 165°, and -6-cyclohexylphenol, m.p. 73–74°; 3 : 5-dinitro-*o*-cresol, m.p. 94°, -anisole, m.p. 69°, and -guaiacol, m.p. 94°; 4-iodo-1 : 3-dinitrobenzene, m.p. 66–67°; Et 3 : 5-dinitrosalicylate, m.p. 78°; 2 : 4 : 2' : 4'-tetranitrodibenzyl, m.p. 136°. M.p. are corr. R. S. C.

Colorimetric determination of small amounts of 2 : 4'-diaminodiphenyl in presence of benzidine. V. ČECH and K. KÁMEN (Chem. Listy, 1939, **33**, 97–101).—2 g. of crude benzidine are dissolved in 150 c.c. of 0.17N-HCl, H₂O is added to 250 c.c., and 25 c.c. of the solution are added to 25 c.c. of boiling H₂SO₄ (*d* 1.36). The solution is cooled to –15°, filtered (from benzidine sulphate) after 20 min., and washed with dil. H₂SO₄ (*d* 1.19) at –15°. To the filtrate + washings are added 20 g. of Na₂CO₃, followed by 4 c.c. of 2.5N-NaNO₂ at 0°, and the solution is diluted to 100 c.c. 5 c.c. of N-NaHCO₃ and 5 drops of 1% Chicago acid are added to 5–10 c.c. of solution or of standard 2 : 4'-diaminodiphenyl solutions, followed by 15 c.c. of H₂O or tetrazotised benzidine solution (0.07 mg. per litre), and the colorations are compared. R. T.

Identification of phenyl alkyl sulphides, sulphoxides, and sulphones. V. N. IPATIEV and B. S. FRIEDMAN (J. Amer. Chem. Soc., 1939, **61**, 684–689; cf. A., 1939, II, 17).—PhAlkS (= X) are usually readily identified by the complexes, X₂PdCl₂. However, PhBu^γS and *tert*-C₆H₁₁Sph give complexes, X₂2PdCl₂, m.p. >250°; with excess of PdCl₂, normal complexes, X₂PdCl₂, m.p. 84° and 72–73°, respectively, are obtained, but these decompose, when kept or recrystallised, into PhAlkS and the abnormal derivatives. Active C₆H₁₁Sph and CHMePr^βSph give oily PdCl₂ complexes. The sulphides are converted into sulphones, nitrated (by 3 : 1 H₂SO₄-HNO₃, except for the *tert*. compounds) to the *m*-NO₂-derivatives, reduced, and acetylated, benzoylated, or *m*-bromobenzoylated, but these products are usually unsuitable for identification. *m*-*p'*-Bromobenzamidolulphones (prep. by *p*-C₆H₄Br·COCl in Et₂O–10% aq. KOH) are, however, sufficiently characteristic. *m*-Aminolulphones with *m*-C₆H₄Br·COBr in NaOH (not the *p*-compound) give the diaroyl derivatives; use of C₆H₅N is usually impractical owing to formation of *m*-bromobenzoic anhydride, m.p. 97–98°. The following are prepared. Complexes, (PhRS)₂PdCl₂, in which R = Et, m.p. 139–140°, Pr^α, m.p. 90–91°, Pr^β, m.p. 162°, CHMeEt, m.p. 137–138°, CHMePr^α, m.p. 107.5–108°, CHEt₂, m.p. 101–102°. Ph *n*-amyl, m.p. 31–32°, CH₂Pr^α·CH₂, m.p. 35.5–36.5° (lit. 37°), and CHEt₂ sulphone, m.p. 46–47°. *m*-NO₂·C₆H₄·CMe₂Et sulphone, m.p. 93–94°. *m*-NH₂·C₆H₄·Bu^β, m.p. 83.5–84°, and CHEt₂ sulphone, m.p. 76–77°. *m*-*m'*-Bromobenzamidophenyl Bu^α, m.p. 130.5–131.5°, CHMeEt, m.p. 115–116°, and *n*-amyl sulphone, m.p. 120.5–121°. *m*-*p'*-Bromobenzamidophenyl CHMeEt, m.p. 141–142°, *n*-, m.p. 165–166°, and iso-amyl, m.p. 168–168.5°, CHMePr^α, m.p. 137–138°, CHEt₂, m.p. 158–159°, and CHMePr^β sulphone, m.p. 128.5–129.5°. *m*-Di-*m'*-bromobenzamidophenyl Bu^α, m.p. 200.5–201.5°, CHMeEt, m.p. 169–170°, Bu^β, m.p. 188–189°, *n*-, m.p. 166.5–168°,

iso-, m.p. 190.5–191.5°, and active amyl, m.p. 175–176.5°, CHMePr^α, m.p. 163.5–164.5°, and CHMePr^β sulphone, m.p. 161–162°. R. S. C.

Colorimetric determination of salicylic acid. G. ILLARI (Annali Chim. Appl., 1938, **28**, 524–529).—Salicylic acid (in concns. >0.001%) is determined spectrophotometrically in solutions containing 0.5% of FeCl₃ and 0.01N. in HCl. F. O. H.

Determination of deoxycholic acid. T. SHIMADA (J. Biochem. Japan, 1939, **29**, 41–50).—A method, based on the colour reaction with PhCHO and 75% H₂SO₄-AcOH (A., 1938, II, 365), is described. F. O. H.

Colorimetric determination of tocopherol (vitamin-E). II. Adsorption experiments. A. EMMERIE and C. ENGEL (Rec. trav. chim., 1939, **58**, 283–289; cf. A., 1939, II, 123, 134).—Tocopherol is separated from carotenoids and vitamin-A by adsorption of the latter on Floridin XS earth (purified by conc. HCl). Al₂O₃ does not effect the separation, but other constituents may be removed. -A preps. react with the FeCl₃-dipyridyl reagent, but behave differently from tocopherol solutions, wheat-germ oil concentrates, or α + β-carotene, with regard to oxidation velocity. A. T. P.

Microchemical alkaloid reactions with a new reagent containing lead iodide. G. H. WAGENAAR (Pharm. Weekblad, 1939, **76**, 276–282).—KOAc solution (1 : 3) is neutralised with AcOH (Me-red) and saturated at the boil with PbI₂. The cooled solution is filtered and contains 5% of PbI₂. It gives characteristic, cryst. ppts. (sensitivity in parentheses) with alypine (1 : 10,000), arecoline (1 : 100), betaine, quinidine (1 : 1250), cocaine (1 : 20,000), cotarnine (1 : 5000), atropine methonitrate, homatropine (1 : 1000), novatropine (1 : 5000), novocaine (1 : 500), pantocaine (1 : 5000), pelletierine, eserine (1 : 200), stovaine (1 : 2000), and sparteine (1 : 750). Amorphous or microcryst. ppts. are obtained with atropine, quinine, cinchonidine, emetine, heroin, hydrastine, hyoscyamine, lobeline, optoquine, percaïne, scopalamine, strychnine, and tutocaine. NHPhAc, aconitine, *p*-NH₂·C₆H₄·SO₂·NH₂, anaesthesine, antipyrine, apomorphine, berberine, brucine, cantharidin, cardiazole, codeine, caffeine, colchicine, dicodide, dionine, ephedrine, ephetonine, β-eucaine, euphylline, morphine, nicotine, orthoform, papavarine, paracodine, phenacetin, pilocarpine, pyramidone, santonin, theobromine, thiocine, urotropine, veratrine, and yohimbine give no ppt. S. C.

Principle for the determination of aminoacids, and its application to collagen and gelatin. M. BERGMANN and W. H. STEIN (J. Biol. Chem., 1939, **128**, 217–232).—A method is described for the accurate determination of NH₂-acids in protein hydrolysates by partial pptn. of each component as a salt, and estimation of the amount still in solution by means of a known solubility product. The hydrolysate of gelatin or collagen was thus found to contain 26.5% of glycine (pptn. by K trioxalochromiate) and 17.5% of *l*-proline (by NH₄ rhodanilate).

A. LI.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1939.

Rôle of free radicals in elementary organic reactions. F. O. RICE and E. TELLER (J. Chem. Physics, 1939, 7, 199).—Errata (cf. A., 1938, II, 425). W. R. A.

Specific gravity change per degree of temperature. L. W. BOSART (Perf. & Essent. Oil Rec., 1939, 30, 145—152).—Determination of d for a large no. of liquid org. compounds indicates a relationship between change in d per degree and chemical constitution. The vals. show that the change is greatest for hydrocarbons, aldehydes, acids, anhydrides, esters, and halogen compounds and smallest for alcohols and esters; *tert.* > *sec.* > primary compounds and unsaturation increases the val. Java citronella oil gives a higher val. than the Ceylon oil and this is assumed to be due to the presence in the former of an unstable form of citronellal or citronellol converted by heat into the more stable form which occurs in the latter. T. F. W.

Review of the chemistry of highly polymerised compounds. H. MARK (Przemysł Chem., 1938, 22, 438—441). R. T.

Preparation and the physical constants of a number of alkanes and cycloalkanes. J. P. WIBAUT [with H. HOOG, S. L. LANGEDIJK, J. OVERHOFF, and J. SMITTENBERG] (Rec. trav. chim., 1939, 58, 329—377).—The following hydrocarbons are prepared in a high degree of purity by methods suitable for the prep. of 1 kg. or more. For each and also for *n*-heptane and $\beta\beta\delta$ -trimethylpentane f.p., b.p. (Cottrell apparatus, corr. to 760 mm.), crit. solution temp. (C.S.T.) with NH_2Ph , n_{D}^{20} , n_{D}^{25} , n_{D}^{30} , d_4^{20} , and γ^{20} are recorded (in most cases also n_{D}^{25} , n_{D}^{30} , d_4^{25} , and d_4^{30} are given). $[R]$ and $[P]$ are calc. Data are given in the order f.p., b.p., C.S.T. *n*-Pentane, —129.7°, 35.95°, 71.7°; β -methylbutane, —160.6°, 27.80°, 78.9°; *n*-hexane, —95.5°, 68.75°, 69.1°; β -methylpentane, glass, 60.30°, 73.9°; γ -methylpentane, glass, 63.30°, 69.3°; $\beta\beta$ -dimethylbutane, —100.5°, 49.70°, 81.2°; $\beta\gamma$ -dimethylbutane, —128.5°, 58.05°, 71.9°; *n*-heptane, —90.8°, 98.40°, 70.1°; β -methylhexane, —118.5°, 90.10°, 73.6°; $\beta\beta$ -dimethylpentane, —124.0°, 79.30°, 78.3°; $\beta\gamma$ -dimethylpentane, glass, 89.80°, 68.0°; $\beta\delta$ -dimethylpentane, —119.1°, 80.60°, 78.7°; $\gamma\gamma$ -dimethylpentane, —135.7°, 86.10°, 69.7°; $\beta\beta\gamma$ -trimethylbutane, —26.3°, 81.00°, 72.2°; *n*-octane, —56.8°, 125.75°, 72.1°; γ -methylheptane, glass, 119.05°, 72.2°; $\beta\gamma$ -dimethylhexane, glass, 115.80°, 70.6°; $\beta\epsilon$ -dimethylhexane, —94.0 109.25°, 78.0°; $\gamma\delta$ -dimethylhexane, glass, 117.85°, 68.0°; $\beta\beta\gamma$ -trimethylpentane, glass, 110.05°, 70.8°; $\beta\beta\delta$ -trimethylpentane, —107.6°, 99.10°, 80.4°; γ -

methyl- γ -ethylpentane (from CHMeEt_2 and ZnEt_2), —91.1°, 118.35°, 65.9°; *n*-nonane, —53.8°, 150.70°, 74.9°; *n*-hexadecane, 17.9°, —, —; ethylcyclobutane, —143.2°, 70.70°, 38.7°; cyclopentane, —94.3°, 49.20°, 17.4°; methylcyclopentane, —142.7°, 71.85°, 34.0°; cyclohexane, 6.4°, 80.80°, 30.4°; methylcyclohexane, —126.4°, 100.80°, 40.3°; isopropylcyclohexane, —89.8°, 154.50°, 48.9°. $\gamma\delta$ -Dimethylhexan- γ -ol (prep. from COMeEt and Mg derivative of CHMeEtBr), b.p. 67.5—69°/16 mm., is described. Ethylcyclobutane is prepared by electrolytic reduction of acetylcyclobutane. S. H. H.

Kinetics of oxidation of methane. I. Intermediate products.—See A., 1939, I, 326.

Oxidation of methane and heavy hydrocarbons by ozone at low temperatures. S. I. SOLOVEITSCHIK (J. Gen. Chem. Russ., 1938, 8, 1696—1698).— CH_2O is produced by oxidation of CH_4 by O_3 at room temp. and at 75—80°. The reaction is not catalysed by Cr-Ni, Pt-black, or Pd-asbestos. R. T.

Reduction of sulphur dioxide by methane.—See A., 1939, I, 333.

Thermal decomposition of ethane by addition of foreign gases.—See A., 1939, I, 326.

Function of free radicals in oxidation of *n*-heptane. R. MAESS (Oel u. Kohle, 1939, 15, 299—306; 321—326).—It is shown qualitatively that the thermal decomp. and the oxidation of *n*- C_7H_{16} can be accelerated by the introduction of free radicals. These are obtained by the thermal decomp. of Me_2N_2 or by the photochemically induced rupture of Me_2N_2 or COMe_2 . Above a certain min. temp. and pressure of *n*- C_7H_{16} the increase of pressure caused by the thermal decomp. of Me_2N_2 is three times as great as that due to the rupture of Me_2N_2 by itself. At these temp. *n*- C_7H_{16} is stable by itself. Under these conditions the reaction is of the second order with respect to the concn. of Me_2N_2 and is independent of $[\text{n-C}_7\text{H}_{16}]$. From the dependence of the reaction in presence of Me_2N_2 on the temp. the energy of activation 50 ± 4 kg.-cal. is derived; this agrees with the literature vals. 47.7 and 51.1 for pure Me_2N_2 . The products of the change include C_3H_8 , C_3H_6 , C_4H_8 , C_4H_6 , and NH_3 so that fission of *n*- C_7H_{16} must be assumed. The photo-oxidations of COMe_2 and of Me_2N_2 are independent of temp. Oxidation of *n*- C_7H_{16} occurs with energy of activation 12.1 and 20.5 kg.-cal. respectively when induced with Me_2N_2 or COMe_2 . The reaction is heterogeneous in part at any rate, since its velocity is very greatly influenced by the nature of the walls of the vessel.

It appears necessary to formulate a chain mechanism since the process at relatively low temp. ($<250^\circ$) takes place explosively after an induction period. Addition of N_2 causes unusual acceleration; rupture of the chains takes place therefore extensively at the walls. Combustion to CO_2 and H_2O does not occur quantitatively. CO in varying proportion and other intermediates are observed. H. W.

Optical rotatory powers of (+)- γ -methyl-n-heptane. J. KENYON and B. C. PLATT (J.C.S., 1939, 633—637).—Rotatory powers for light of various λ in the visible spectrum are determined for (+)- γ -methyl-n-heptane [(+)-methylethyl-n-butylmethane] (I), b.p. $115-118^\circ$. In homogeneous condition, vals. of $[\alpha]$ are const. from 18° to 49° , suggesting no marked association. In CH_2Cl_2 , C_6H_6 , or CS_2 , vals. of $[\alpha]$ change, e.g., 10% when concn. of solute varies from 4.4 to 2.2%. Thus even non-polar solvents do not act as inert diluents. α - or β -Ethyl-n-hexanol and aq. alkaline $KMnO_4$ afford *dl*-n-heptane- γ -carboxylic acid, which gives the (–)-acid (II), b.p. $218-220^\circ$ (quinine salt, m.p. $64-65^\circ$, $[\alpha]_{5893} -112.0^\circ$ in EtOH), and the (+)-acid, b.p. $218-220^\circ$ (cinchonidine salt, m.p. $67-69^\circ$, $[\alpha]_{5893} -74.8^\circ$ in EtOH) [Et ester (III), b.p. $96-97^\circ/35$ mm.]. (III) and aq. NaOAc–Na–Et₂O at 0° , kept slightly acid with 80% AcOH (Prins' method; alkaline media are avoided), give esters, b.p. $84-92^\circ/18$ mm. and $117-137^\circ/3$ mm., the former being hydrolysed by aq. NaOH–EtOH to (+)- β -ethyl-n-hexanol (IV), b.p. $92-94^\circ/22$ mm.; red P and I at 150° give the -hexyl iodide, b.p. $100-103^\circ/18$ mm., converted by Zn–AcOH into (I). n-Bu *dl*-n-heptane- γ -carboxylate (prep. by Fischer–Speier method) has b.p. $110-111^\circ/18$ mm., the corresponding isoamyl ester, b.p. $120-121^\circ/16$ mm., and the Ph ester, b.p. $138-141^\circ/12$ mm. (from acid chloride and $PhOH \cdot C_5H_5N$); the three esters are reduced by Na and Bu, isoamyl, and Et alcohol, respectively. *dl*- β -Ethyl-n-hexanol gives a *dl*- β -ethyl-n-hexyl H phthalate, m.p. $14-16^\circ$. Decomp. of brucine β -ethyl-n-hexyl phthalate yields a H phthalate $[\alpha]_{5461} +1.73^\circ$ in CS_2 , hydrolysed to (–)- β -ethyl-n-hexanol, b.p. $178-179^\circ$. Vals. of $[\alpha]$ at various temp. and in solvents are recorded for (II) and its Et ester and (IV). A. T. P.

Catalytic exchange of deuterium and hydrogen in hydrocarbons.—See A., 1939, I, 329.

Polymerides of propylene from isopropyl alcohol and boron trifluoride. F. C. WHITMORE and J. F. LAUCIUS (J. Amer. Chem. Soc., 1939, 61, 973—974).— Pr^3OH and BF_3 at 100° give 20% of tetrapropylene, b.p. $94-105^\circ/30$ mm. R. S. C.

Reactions of Δ^2 -hexene. I. Reactions with sulphuric acid, halogens, and halogen acids. L. SPIEGLER and J. M. TINKER (J. Amer. Chem. Soc., 1939, 61, 940—942).— $(CH_2Et)_2$ and 87% H_2SO_4 at 20° give a mixture, hydrolysed by hot, dil. H_2SO_4 to n-hexan- γ -ol (60%), b.p. $134-138^\circ$, with some $\gamma\delta$ -epoxy-n-hexane, b.p. $105-106^\circ$, and polymerides (12%), $(C_6H_{12})_n$ ($n = 2-5$). Cl_2 , SO_2Cl_2 , or PCl_5 converts $(CH_2Et)_2$ into $\gamma\delta$ -dichloro-n-hexane, b.p. $69-70^\circ/30$ mm., and higher chlorinated products. Dry HBr and $(CH_2Et)_2$ in $CHCl_3$ give CH_2EtPr^2Br ,

b.p. $68^\circ/50$ mm., $141-142^\circ/760$ mm., converted by NaCNS in EtOH into γ -thiocarbamido-, b.p. $121^\circ/40$ mm., and by NaSH–EtOH into γ -thiol-n-hexane, b.p. $57^\circ/20$ mm. Dry HCl does not react with $(CH_2Et)_2$ at -20° or room temp., but conc., aq. HCl at room temp. yields γ -chloro-n-hexane, b.p. $59.5-60^\circ/95$ mm. R. S. C.

Thermo-polymerisation of n-octene.—See A., 1939, I, 326.

Action of sodium with pinacolin. I. Unsymmetrical ditert.-butylbutadiene. H. J. BACKER (Chem. Weekblad, 1939, 36, 205—208).—A solution of pinacolin in PhMe treated with Na and then with H_2O affords a mixture of unsaturated alcohols and ketones which give a good yield of $CH_2Bu^t \cdot CH \cdot CBu^t \cdot CH_2$ (I) when successively reduced with $Al(OPr^i)_3$ and dehydrated with $H_2C_2O_4$. (I) with SO_2 forms the corresponding cyclic sulphone, hydrogenated to $\alpha\gamma$ -ditert.-butylbutane $\alpha\delta$ -sulphone, m.p. $76-76.5^\circ$, and oxidised with $KMnO_4$ to the $\beta\gamma$ -diol, m.p. 192.5° , converted by $Pb(OAc)_4$ into the corresponding cyclic ketol sulphone (II), m.p. $82-83^\circ$ (acetate, m.p. 106° ; chloride, m.p. 156°). The ring in (II) is opened with alkalis, forming HCO_2H and $CH_2Bu^t \cdot SO_2 \cdot CH_2 \cdot COBu^t$, m.p. 79.5° (enol Me ether, m.p. $30-32^\circ$). The β -ketol, $COBu^t \cdot CH_2 \cdot CMeBu^t \cdot OH$ (2:4-dinitrophenylhydrazone, m.p. 148°), is reduced with Na and EtOH to $\alpha\gamma$ -ditert.-butylbutane- $\alpha\gamma$ -diol, m.p. $90-91^\circ$, which is converted into (I) by heating with I, and dehydrogenated to an unsaturated ketone, b.p. $85-87^\circ/12$ mm. (2:4-dinitrophenylhydrazone, m.p. 147°). S. C.

Methylgeraniolene and its pyrolysis. J. DŒUVRE (Bull. Soc. chim., 1939, [v], 6, 882—889; cf. A., 1936, 311).—Geraniol or linalol with liquid NH_3 –Na–EtOH gives methylgeraniolene [$\beta\gamma$ -dimethyl- Δ^2 -octadiene] (I), b.p. $79-80^\circ/30$ mm., $167-168^\circ/745$ mm. (other consts. given). Pyrolysis at $570-580^\circ/140$ mm. gives isoprene and $CMe_2 \cdot CHMe$ (approx. 2:1), and probably also γ -methyl- Δ^2 -pentene, γ -methyl- Δ^2 -butene, and β -methylpropene. Ozonolysis of (I) in aq. AcOH gives EtOH, CO_2Me , and lœvulaldehyde. A. T. P.

Decomposition of acetylene in sulphuric acid.—See A., 1939, I, 327.

Graphitic oxide.—See A., 1939, I, 332.

Replacement of aliphatically united bromine by lithium by means of lithium phenyl. III. G. WITTIG and U. PÖCKELS (Ber., 1939, 72, [B], 884—886).—LiPh and $CHBr_3$ in Et_2O at 0° give PhBr, with a little PhOEt and stilbene. The mechanism of the change is not obvious. H. W.

Photochemical bromination of trans-dichloroethylene and bromine-sensitised photodecomposition of dichlorodibromoethane.—See A., 1939, I, 330.

Reactions of tertiary bases with polyhalogeno-paraffins. W. C. DAVIES, (MISS) E. B. EVANS, and H. R. WHITEHEAD (J.C.S., 1939, 644—646).—Vals. of d , n , and η of binary mixtures of $NPhMe_3$ and CH_2Cl_2 or $CHCl_3$ show little variation from ideal behaviour. Deviations in η can be explained by association. Similarly, cryoscopic or ebullioscopic

measurements give no indication of unusual behaviour. NMe_3 and NEt_3 , however, in presence of air or O_2 , react readily with CHBr_3 , (CHCl_3) and CCl_4 do not react) giving the hydrobromide of the base and CH_2O or MeCHO , respectively. CBr_4 and NMe_3 give CH_2O and a solid, m.p. 209–210° (decomp.) (cf. Zellhoefer *et al.*, A., 1938, I, 394; Hammick *et al.*, A., 1939, I, 25).

A. T. P.

Resolution of inactive alcohols by means of their esters with tartranilic acid. F. BARROW and R. G. ATKINSON (J.C.S., 1939, 638–640).— NH_2Ph and an almost saturated hot aq. solution of (+)-tartaric acid afford (+)-tartranil, m.p. 257° (decomp.), $[\alpha]_{\text{D}}^{20} +130^\circ$ in MeOH, which with β -n-amyl alcohol and conc. H_2SO_4 at 100° (16 hr.) gives (–)- β -n-amyl (+)-tartranilate, m.p. 114°, $[\alpha]_{\text{D}}^{20} +76.9^\circ$ (const.) in EtOH, hydrolysed by 20% aq. KOH to (–)- β -n-amyl alcohol, b.p. 119–120°, $[\alpha]_{\text{D}}^{15} -13.4^\circ$ (cf. (+)-alcohol; Pickard and Kenyon, J.C.S., 1911, 99, 45). MgBuBr and MeCHO give β -n-hexyl alcohol (66% yield) (*loc. cit.*), converted into (–)- β -n-hexyl (+)-tartranilate, m.p. 124°, $[\alpha]_{\text{D}}^{18} +93.3^\circ$ in EtOH, and thence into (–)- β -n-hexyl alcohol, b.p. 136–137°, $[\alpha]_{\text{D}}^{18} -13.48^\circ$ [cf. (+)-alcohol, *loc. cit.*]. Similarly prepared are: (–)- β -n-octyl, m.p. 126°, $[\alpha]_{\text{D}}^{20} +70.9^\circ$ in EtOH (const.) [(–)- β -n-octyl alcohol, b.p. 95°/25 mm., $[\alpha]_{\text{D}}^{20} -9.7^\circ$], (–)-menthyl, m.p. 131°, $[\alpha]_{\text{D}}^{20} +29.85^\circ$ in EtOH [(–)-menthol, m.p. 43°, b.p. 89°/2 mm., $[\alpha]_{\text{D}}^{20} -51.4^\circ$ in EtOH], and β -methyl-n-butyl (+)-tartranilate (I), m.p. 123–124°, $[\alpha]_{\text{D}}^{17} +111.2^\circ$ in EtOH (const.). (I) gives only a partly active β -methyl-n-butyl alcohol, b.p. 130°, $[\alpha]_{\text{D}}^{18} +3.75^\circ$. Complete resolution of the tartranilate of CHMeEt-OH also failed, due to formation of mixed crystals of the diastereoisomeric esters. (I) and Br-AcOH give the corresponding (+)-p-bromotartranilate, m.p. 144°, $[\alpha]_{\text{D}}^{19} +95.6^\circ$ in EtOH (const.), hydrolysed to $p\text{-C}_6\text{H}_4\text{Br-NH}_2$ and (–)- β -methyl-n-butyl alcohol, b.p. 130°, $[\alpha]_{\text{D}}^{18} -1.31^\circ$. The ester from the more sol. fractions had $[\alpha]_{\text{D}}^{19} +90.4^\circ$ in EtOH, and gives an alcohol, $[\alpha]_{\text{D}}^{22} +1.50^\circ$. β -n-Bu (+)-tartranilate, m.p. 128°, $[\alpha]_{\text{D}}^{18} +119.7^\circ$ (const.) in EtOH, affords a feebly active β -butyl alcohol, $[\alpha]_{\text{D}}^{18} -0.27^\circ$. Optically pure (+)- β -butyl alcohol gives (+)- β -Bu (+)-tartranilate, m.p. 128°, $[\alpha]_{\text{D}}^{20} +134.3^\circ$ in EtOH, a much higher val. than for any prepared from the inactive alcohol. Tartranilates were not obtained from α -terpineol and CHPhMe-OH .

A. T. P.

Aliphatic difluorides. A. L. HENNE, (Miss) M. W. RENOLL, and H. M. LEICESTER (J. Amer. Chem. Soc., 1939, 61, 938–940).—Propylidene, b.p. 7–8°, and n-heptylidene difluoride, b.p. 119.7°, are obtained in >80% yield from the chlorides by HgF_2 , but not by SbF_3 . $\beta\beta$ -Difluoro-propane, b.p. –0.6° to –0.2°, n-butane, b.p. 30.8°, and n-pentane, b.p. 59.8°, are readily obtained from the corresponding chlorides by SbF_3 , best with a little SbF_5 . Cl_2 in sunlight leads smoothly to $\alpha\alpha\beta\beta\gamma$ -hexachloro- $\gamma\gamma$ -difluoro-, m.p. 50.8°, and $\alpha\alpha\gamma\gamma\gamma$ -hexachloro- $\beta\beta$ -difluoro-propane, m.p. –12.9°, $\alpha\alpha\beta\beta\delta\delta\delta$ -octachloro- $\gamma\gamma$ -difluoro-n-butane, m.p. –2° to –1°, and $\alpha\alpha\beta\beta\gamma\gamma\epsilon\epsilon\epsilon$ -decachloro- $\delta\delta$ -difluoro-n-pentane, m.p. 10–15°. Complete chlorination is thus made easier by the presence of F. All

these halides are stable, but at 250° the asymmetrical are more stable than the symmetrical. Asymmetry leads to higher m.p. Nearly pure $\text{CCl}_3\text{-CEtF}_2$, m.p. –58–60°, and $\text{CCl}_3\text{-CPr}^i\text{F}_2$, m.p. –52°, are obtained as intermediates. Prep. of CMeEtCl_2 , $\text{CMePr}^i\text{Cl}_2$, CHEtCl_2 , b.p. 88.3°, CHPr^iCl_2 , and $n\text{-C}_6\text{H}_{13}\text{-CHCl}_2$ is described.

R. S. C.

Condensing action of nickel- and cobalt-thorium catalysts with aliphatic alcohols. N. P. MASINA (J. Gen. Chem. Russ., 1938, 8, 1281–1285).—EtOH or PrOH passed over Ni-Th or Co-Th catalysts at 220° yields acetals, esters, and aldehydes, with small amounts of AcOH or EtCO_2H .

R. T.

Action of bromine on ethylenic glycols. J. S. SALKIND and A. I. NOGAIDELI (J. Gen. Chem. Russ., 1938, 8, 1816–1822).— $(\text{OH-CHPh-CH})_2$ and Br in CHCl_3 at –12° yield an unstable dibromide, which eliminates HBr at room temp., affording 3-bromo-2:5-diphenyl-2:5-dihydrofuran, an oil, which with 25% K_2CO_3 at 70°, or with AgOAc in AcOH (90–108°), yields only small amounts of unidentified products; 3-iodo-2:5-diphenyl-2:5-dihydrofuran, an oil, is obtained similarly. $(\text{OH-CMePr}^i\text{-CH})_2$ similarly yields 3-bromo-2:5-dimethyl-2:5-diisopropyl-2:5-dihydrofuran, an oil. $(\text{OH-CHMe-CH})_2$ (I) and Br in CHCl_3 at –5° afford $\gamma\delta$ -dibromohexane- $\beta\epsilon$ -diol, m.p. 138.5–140°, and 3:4-dibromo-2:5-dimethyltetrahydrofuran, an oil, converted by vac. distillation into 3-bromo-2:5-dimethyl-2:5-dihydrofuran, b.p. 48–51°/5 mm. (OAc-CHMe-C) $_2$ and H_2 (Pd catalyst) yield two optical isomerides of $\beta\epsilon$ -diacetoxy- Δ^7 -hexene, b.p. 86–87°/4 mm. and 94–96°/4 mm.; these isomerides are further hydrogenated to two different forms of $(\text{OAc-CHMe-CH}_2)_2$. The isomeride of b.p. 86–87°/4 mm. with Br gives γ -bromo- $\beta\epsilon$ -diacetoxy- Δ^7 -hexene, b.p. 92–96°/6 mm.

R. T.

Action of sodium with pinacolin. II. Pinacols from pinacolin and $\beta\gamma$ -ditert.-butylbutadiene. H. J. BACKER (Chem. Weekblad, 1939, 36, 214–219; cf. A., 1939, II, 238).—The product (I), m.p. 74.5°, obtained in 8% yield by treating pinacolin in Et_2O with Na and H_2O is an equimol. compound of two isomeric $\beta\gamma$ -ditert.-butylbutane- $\beta\gamma$ -diols, m.p. 69° (II) and 88° (III) respectively. (II) is obtained by interaction of MgMeI and $(\text{COBu}^t)_2$ and (III) by treating (I) with acids. On further treatment with acids the diols give pinacolin, $(\text{CMe}_2)_2$, and $\beta\gamma$ -ditert.-butylbutadiene, b.p. 180° (Br_2 -derivative, m.p. 96–97.5°), which is hydrogenated to the H_2 -derivative (IV) and $(\text{CHMeBu}^t)_2$, b.p. 191–192°, and fails to react with SO_2 or maleic anhydride. These reactions are explained on stereochemical grounds which are fully discussed. With O_3 or BzO_2H (IV) affords an epoxide, $\text{C}_{12}\text{H}_{24}\text{O}$ (2:4-dinitrophenylhydrazones, m.p. 172°), which when treated with acids is isomerised and oxidised to $\alpha\beta$ -ditert.-butylbutyric acid, m.p. 94–95°.

S. C.

Hydrogenation of acetylenic compounds. XXX. Catalytic hydrogenation of dimethyldiisopropylhexinediol. J. S. SALKIND and A. I. NOGAIDELI (J. Gen. Chem. Russ., 1938, 8, 1382–1384).—A solution of Mg in $\text{EtBr-Et}_2\text{O}$ saturated with C_2H_2 when added to COMePr^i yields $\beta\gamma\eta$ -

tetramethyl- Δ^8 -octene- γ - ζ -diol, m.p. 78—80°, which is hydrogenated (Pd catalyst) to β - γ - ζ -tetramethyl- Δ^8 -octene- γ - ζ -diol, b.p. 119—121°/7—8 mm. R. T.

Benzoylation of *d*-sorbitol and meso-erythritol. S. HANAI (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 1224—1235).—Examination of the decomposition products of partly benzoylated *d*-sorbitol and meso-erythritol shows that primary OH are more easily substituted than *sec*. A. Li.

α - γ -Trialkoxybutanes. R. O. NORRIS, J. J. VERBANC, and G. F. HENNION (J. Amer. Chem. Soc., 1939, 61, 887).— $\text{Hg}(\text{BF}_3 \cdot \text{O} \cdot \text{Me})_2$, prepared by warming $\text{BF}_3 \cdot \text{Et}_2\text{O}$, red HgO , and a little $\text{CCl}_3 \cdot \text{CO}_2\text{H}$ in MeOH , catalyses addition of ROH to $\text{CH}_2 \cdot \text{CH} \cdot \text{C} \cdot \text{CH}$ at 40° to yield α - γ -tri-ethoxy- (I), b.p. 70—71°/5 mm., -*n*-butoxy- (II), b.p. 120°/3 mm., and -*n*-propoxy-butane, b.p. 118—120°/7 mm. Hot Ac_2O converts (I) into AcOH (93%), EtOAc (95%), $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{C} \cdot \text{Me} \cdot \text{OEt}$ (56%), and much polymeride. Ac_2O and (II) give similarly BuOAc (90%), AcOH , and $\text{OBu} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{C} \cdot \text{Me} \cdot \text{OBu}$. R. S. C.

Thermal analysis of binary systems containing glycerol trinitrate.—See A., 1939, I, 264.

X-Ray and thermal examination of the glycerides. V. Unsymmetrical mixed triglycerides, $\text{COR} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{O} \cdot \text{COR}') \cdot \text{CH}_2 \cdot \text{O} \cdot \text{COR}'$. M. G. R. CARTER and T. MALKIN (J.C.S., 1939, 577—581; cf. A., 1939, II, 97).—The unsymmetrical mixed glycerides are prepared by acylation of α -monoglycerides in $\text{C}_6\text{H}_5 \cdot \text{C}_5\text{H}_5\text{N}$ at room temp. (cf. A., 1934, 720) and are short, thick prisms as compared with the long, slender, thin prisms of the symmetrical. Glycerides are examined in which R' is shorter than R , viz., α -decodilaurin (I), α -laurodimyristin (II), α -myristodipalmitin (III), and α -palmitodistearin (IV); and R' is longer than R , viz., α -laurodidodecin (V), α -myristodilaurin (VI), α -palmitodimyristin (VII), and α -stearodipalmitin (VIII). All exist in four solid modifications, viz., vitreous, α , β' and β , in order of increase in m.p., thus, (I) 5°, 26°, 31°, 35.5°; (II) 22°, 37°, 42°, 46.5°; (III) 36°, 47.5°, 52°, 57°; (IV) 50°, 57°, 61°, 65°; (V) 0°, 17.5°, 26°, 30°; (VI) 19°, 33.5°, 39°, 43.5°; (VII) 34°, 45.5°, 50.5°, 54°; (VIII) 46.5°, 55°, 59.5°, 62.5°. Transitions from lower to higher m.p. are less rapid ($\beta' \rightarrow \beta$ is very slow) than those of the symmetrical mixed triglycerides. The latter melt a few degrees higher than the corresponding unsymmetrical compounds (cf. King *et al.*, A., 1934, 755). X-Ray examinations (except vitreous) are recorded and discussed. A. T. P.

Reaction of divinyl sulphide with silver oxide. W. L. RUGH and A. E. ERICKSON (J. Amer. Chem. Soc., 1939, 61, 915—916).—In contradiction to Semmler (A., 1887, 1089), divinyl sulphide [prep. from $(\text{CH}_2\text{Br} \cdot \text{CH}_2)_2\text{S}$ by KOH in aq. EtOH], b.p. 83.5—84°/759 mm., does not give $(\text{CH}_2 \cdot \text{CH})_2\text{O}$ when heated with Ag_2O (in one experiment an explosion occurred) and with moist Ag_2O it gives no MeCHO . R. S. C.

Sulphur alkyl iodides or sulphenyl iodides. H. RHEINBOLDT and E. MOTZKUS [with, in part, M. SCHULTE and F. MOTT] (Ber., 1939, 72, [B], 657—667).—The prep. of alkylsulphenyl iodides can

be achieved if a *tert.* alkyl radical is involved. $(\text{Bu}^\text{t}\text{S})_2\text{Hg}$ or $\text{Bu}^\text{t}\text{S} \cdot \text{Ag}$ and I in well-cooled Et_2O afford *tert.*-butylsulphenyl iodide (I), which forms an orange-red solution with a characteristic penetrating odour. It is stable for some hr. in well-cooled Et_2O and by rapidly working at a sufficiently low temp. it can be obtained mixed with only a small proportion of the disulphide (II). The ethereal solution is only slowly decomposed by H_2O , mainly with production of (II), I, and a strongly acid solution. Similarly, aq. $\text{Na}_2\text{S}_2\text{O}_3$ reacts slowly, particularly in the dark. With activated Mg or Hg , solutions of (I) yield (II) almost quantitatively. Pure NaOMe or NaOEt reacts rapidly with production of sulphenic esters. NH_2Me gives $\text{NH}_2\text{Me} \cdot \text{HI}$ and *tert.*-butylsulphenylmethanamide, b.p. 56.5°/58 mm., ~124° (slight decomp.)/atm. pressure (*m*-nitrobenzoyl derivative, m.p. 120—121° after softening at 119°). *tert.*-Butylsulphenyl-dimethylamide and -piperidide, b.p. 78—79°/14 mm., and ditert.-butylsulphenylpiperazide, m.p. 120°, are described. *tert.*-Amylsulphenylpiperidide has b.p. 100°/12 mm. $(\beta\text{-C}_{10}\text{H}_7\text{S})_2\text{Hg}$ and (I) afford 2:2'-dinaphthyl disulphide and 2-naphthyl Bu^t disulphide, m.p. 52.8—53.3° after softening at 52°, also obtained by use of $\beta\text{-C}_{10}\text{H}_7\text{SH}$ or from $\text{Bu}^\text{t}\text{SH}$ and $\beta\text{-C}_{10}\text{H}_7\text{S} \cdot \text{CNS}$. $\alpha\text{-C}_{10}\text{H}_7\text{SH}$ and (I) afford a solution which is immediately decolorised by $\text{Na}_2\text{S}_2\text{O}_3$. $(\text{O} \cdot \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S})_2\text{Hg}$ and I yield the corresponding disulphide. H. W.

Existence of aliphatic sulphenyl chlorides and bromides. H. RHEINBOLDT and F. MOTT (Ber., 1939, 72, [B], 668—670).—Sulphenyl chlorides and bromides do not appear preparable according to the scheme: $\text{CR}_3 \cdot \text{SH}$ (I) + $\text{X}_2 \rightarrow \text{CR}_3 \cdot \text{SX}$ (II) + HX ; (I) + (II) $\rightarrow \text{CR}_3 \cdot \text{S} \cdot \text{S} \cdot \text{CR}_3$ (III) + HX ; (III) + $\text{X}_2 \rightleftharpoons 2\text{CR}_3 \cdot \text{SX}$. Br and $(\text{Bu}^\text{t}\text{S})_2\text{Hg}$ in Et_2O react, $(\text{Bu}^\text{t}\text{S})_2\text{Hg} + 2\text{Br}_2 \rightarrow 2\text{Bu}^\text{t}\text{SBr} + \text{HgBr}_2$. The resulting orange-red solution does not contain free Br and is not immediately decolorised by $\text{Na}_2\text{S}_2\text{O}_3$. The presence of $\text{Bu}^\text{t}\text{SBr}$ is established by the formation of *tert.*-butylsulphenylpiperazide (IV) on addition of piperazine. The analogous reaction with Cl_2 gives an ill-defined result. *tert.*-Butylsulphenyl-dimethylamide reacts immediately with HBr or HCl thus: $\text{Bu}^\text{t}\text{S} \cdot \text{NMe}_2 + 2\text{HX} = \text{Bu}^\text{t}\text{SX} + (\text{NH}_2\text{R}_2)\text{X}$. The formation of the chloride is demonstrated by the isolation of (IV) from the solution. H. W.

Allylthiophosphoryl chloride. V. M. PLETZ (J. Gen. Chem. Russ., 1938, 8, 1296—1297).— PCl_5 and H_2S in CS_2 yield PSCl_3 , which with $\text{CH}_2 \cdot \text{CH} \cdot \text{OH}$ (3 hr. at 100°) gives $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{PSCl}_2$, with $(\text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{O})_2\text{PSCl}$ and $(\text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{O})_3\text{PS}$. R. T.

Mechanism of the Kolbe electrosynthesis and allied reactions.—See A., 1939, I, 271.

Preparation of esters from aqueous alcohols and acids in presence of aluminium chloride hexahydrate. II. A. N. AKOPJAN (J. Gen. Chem. Russ., 1938, 8, 1763—1765).—Esters are obtained by boiling aq. alcohols (MeOH , EtOH , $\text{C}_5\text{H}_{11}\text{OH}$) with acids (AcOH , BzOH) under reflux with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The yields fall with increasing $[\text{H}_2\text{O}]$, and rise with increasing $[\text{AlCl}_3]$. R. T.

Lead acetato-halides.—See A., 1939, I, 333.

Photolysis of acetyl bromide.—See A., 1939, I, 330.

Preparation of lead tetra-acetate. R. E. OESPER and (Miss) C. L. DEASY (J. Amer. Chem. Soc., 1939, 61, 972—973).—Prep. of $\text{Pb}(\text{OAc})_4$ is improved. R. S. C.

Reformatsky reaction. Efficient procedure for the preparation of bromoacetic ester in large quantities. S. NATELSON and S. P. GOTTFRIED (J. Amer. Chem. Soc., 1939, 61, 970—971).—The Reformatsky reaction is best (>60—70% yield) effected at 90—105°, e.g., in 1:1 C_6H_6 -PhMe. Dehydration is best effected by dry HCl. Prep. of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ is described. R. S. C.

Esters of organic acids from ethylenic hydrocarbons. T. D. ALDOSCHIN (J. Gen. Chem. Russ., 1938, 8, 1385—1389).—Olefines heated at 100° with org. acids in presence of ZnCl_2 yield the appropriate esters. Thus $(\text{CHMe})_2$, $\text{CHMe}\cdot\text{CHEt}$, or $\text{CHMe}\cdot\text{CHBu}^a$ and AcOH yield respectively $\text{CHMeEt}\cdot\text{OAc}$, $\text{CHMePr}^a\cdot\text{OAc}$, and $\text{CHMeBu}^a\cdot\text{OAc}$. sec.-Amyl, b.p. 177—178°, and sec.-Bu chloroacetate, b.p. 163—164°, are prepared analogously. R. T.

Saponification of the trichloroacetic esters.—See A., 1939, I, 327.

Ozonisation of acrylic and crotonic acid and of their ethyl esters. E. BRINER and D. FRANCK (Helv. Chim. Acta, 1939, 22, 587—591; cf. A., 1938, II, 428).—Ozonisation of acrylic acid (I) in H_2O gives a slight deficit of CH_2O and a considerable shortage of $\text{H}_2\text{C}_2\text{O}_4$ and HCO_2H ; these observations and a marked evolution of CO_2 show that much of the ozonide is destroyed. Ozonisation of (I) in MeOH at -60° causes somewhat less extensive decomp. Scission of the ozonide of Et acrylate gives CH_2O and EtHC_2O_4 but considerable destruction is observed, particularly when treatment is effected with warm H_2O under pressure. Ozonisation of crotonic acid (II) gives aldehyde, probably $\text{CHO}\cdot\text{CO}_2\text{H}$, in amount nearly equiv. to that of the O_3 consumed. Destruction of the ozonide with evolution of CO_2 affects that part of the mol. which would normally yield AcOH . The formation of H_2O_2 is merely a subsidiary change. During the ozonisation of Et crotonate in CCl_4 there is no appreciable evolution of CO_2 , which is observed when the ozonide is treated with H_2O . The amount of H_2O_2 is < that produced from (II). The main products are MeCHO and EtHC_2O_4 . H. W.

Analogies between electrolytic and chemical methods of reduction. Experiments with sorbic acid. Mechanism. C. L. WILSON (Trans. Electrochem. Soc., 1939, 75, Preprint 17, 203—215).—Electrolytic reduction of sorbic acid at prepared Ni and Pt cathodes is of a catalytic nature, giving Δ^a -hexenoic and hexoic acid, whilst other metallic cathodes, dissolving metals, and couples yield a mixture of Δ^b - and Δ^c -hexenoic acid (I), with, in presence of Hg, a pinacol; of this mixture 39—45% is (I) in alkaline (sorbate ion) and 50—54% in acid solution, but the proportion is independent of the metal employed. The mechanism of reduction is

discussed. The formation of pinacol is regarded as involving a heterogeneous process favoured at liquid cathodes, exemplified by greater formation at a Ga cathode above the m.p. F. R. G.

Calcium oleate.—See A., 1939, I, 317.

Electrochemical experiments with various organic acids.—See A., 1939, I, 271.

Catalytic hydrogenation of organic acids in alkaline solution. B. B. ALLEN, B. W. WYATT, and H. R. HENZE (J. Amer. Chem. Soc., 1939, 61, 843—846).— α - and γ -OH-acids are resistant to hydrogenation as Na salts in 5% aq. NaOH in presence of Raney Ni at 250°, but β -OH-acids give $\text{CH}_2\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ at 175° (doubtless by way of $\text{CHR}\cdot\text{CH}\cdot\text{CO}_2\text{H}$). Thus, $\text{COMe}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ at 100° gives $\text{OH}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ (not further reduced at 250°); AcCO_2H at 60° gives lactic acid (not further reduced at 250°); maleic or *dl*-malic acid gives $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ at 100° and 175°, respectively; and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ gives EtCO_2H at 175°. Tartaric acid at 235° gives lactic acid, probably by way of $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ and AcCO_2H . HCO_2H at 250° reacts thus: $2\text{HCO}_2\text{Na} + 2\text{H}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CH}_4 + \text{H}_2\text{O}$. Aconitic acid at 100° gives tricarballic acid. $\text{H}_2\text{C}_2\text{O}_4$ is stable at 250°. R. S. C.

Ether-like compounds. IV. Preparation of 1:3-dioxol-5-ones. E. J. SALMI and A. POHJOLAINEN (Ber., 1939, 72, [B], 798—803).—The following compounds are described: methylene α -hydroxy-*n*-butyrate $\begin{matrix} \text{CHEt}\cdot\text{O} \\ \text{CO}\text{---}\text{O} \end{matrix} > \text{CH}_2$, b.p. 165—166.2°/760 mm., α -hydroxyisovalerate, b.p. 172.2—173.4°/756 mm., α -hydroxyisohexzoate, b.p. 84.0—86.0°/9 mm., α -hydroxy- α -methylvalerate, b.p. 62.0—62.2°/3 mm., cyclopentan-1-ol-1-carboxylate, b.p. 96.2—96.6°/17 mm., and cyclohexan-1-ol-1-carboxylate, b.p. 114.8—115.2°/21 mm.; ethylidene cyclopentan-1-ol-1-carboxylate, b.p. 94.1°/15 mm., and cyclohexan-1-ol-1-carboxylate, b.p. 101.5—103°/15 mm.; benzylidene α -hydroxyisobutyrate, b.p. 134.5—135.3°/12 mm.; furfurylidene, b.p. 105.3—106.2°/5 mm., and cyclopentylidene, b.p. 82—83°/7 mm., α -hydroxyisobutyrate; cyclopentylidene α -hydroxy- α -methylbutyrate, b.p. 89—92°/5—6 mm.; cyclohexylidene α -hydroxyisobutyrate, b.p. 109.0—110.0°/17 mm., α -hydroxy- α -methylbutyrate, b.p. 123—125°/16 mm., and cyclohexan-1-ol-1-carboxylate, b.p. 150—152°/15 mm. H. W.

Preparation of *tert*-butylmalonic acid from neopentyl chloride. M. T. BUSH (J. Amer. Chem. Soc., 1939, 61, 965).— $\text{CH}_2\text{Bu}^n\cdot\text{MgCl}$ in $\text{Et}_2\text{O}\cdot\text{N}_2$ is treated with CO_2 at -5°, then with MgEtBr , and finally again with CO_2 . 5-7% of $\text{CHBu}^n(\text{CO}_2\text{H})_2$ and 22% of $\text{CH}_2\text{Bu}^n\cdot\text{CO}_2\text{H}$ are obtained. R. S. C.

Crystal-liquid equilibria in mixtures containing antipodes of dichlorosuccinic acid and of lactamide.—See A., 1939, I, 265.

β -isoPropylglutaconic acid. S. K. RANGA NATHAN (J. Indian Chem. Soc., 1939, 16, 67—70).— Pr^iCOCl (prep. by PCl_3 at 0°) and $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ in Et_2O at <0° give a good yield of $\text{COPr}^i\text{CHAc}\cdot\text{CO}_2\text{Et}$, b.p. 100°/6 mm., hydrolysed by 10% aq. NH_3 at 40° to $\text{COPr}^i\text{CH}_2\cdot\text{CO}_2\text{Et}$, b.p.

72°/3 mm. (*semicarbazone*, m.p. 103°). This with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and KOEt gives 20% of *Et* α -cyano- β -isopropylglutaconate, b.p. 145°/3 mm. (only 5% obtained by use of NaOEt), which is hydrolysed by conc. HCl to (? *trans*-) β -isopropylglutaconic acid (I), m.p. 142° (5–10%), and 2:6-dihydroxy-4-isopropylpyridine (large amount). With AcCl (I) gives the *OH-anhydride*, $\text{CPr}^3\langle\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{OH}) \\ \text{CH}-\text{CO} \end{smallmatrix}\rangle\text{O}$, an oil, which yields the mono-*p*-toluidide, m.p. 150°, or, by 30% KOH at 35°, the (? *cis*-)*acid*, m.p. 129.5–130.5°.

R. S. C.

Treatment of 0: λ -trihydroxystearic acids with acetone. V. I. ESAFOV and Z. I. TORGASCHINA (J. Gen. Chem. Russ., 1938, 8, 1594–1596).—Of the two isomerides of 0: λ -trihydroxystearic acid, that of m.p. 110–111° gives with COMe_2 quant. yields of λ -hydroxy-0: λ -isopropylenedioxystearic acid, an oil, whilst the isomeride of m.p. 139–141° does not combine with COMe_2 under the given conditions. Presence of corresponding 0: λ -OH-groups in the former, but not the latter, case is postulated.

R. T.

Deuterium compounds. Preparation of glyoxal- d_2 , *trans*-ethylene- d_2 -dicarboxylic acid and *dl*- α - β -dihydroxyethane- d_2 - α - β -dicarboxylic acid. H. ERLNMEYER, O. BITTERLIN, and H. M. WEBER (Helv. Chim. Acta, 1939, 22, 701–706).— $\text{C}_2(\text{CN})_2$ can be obtained in only small yield from C_2I_2 . Reduction (PtO_2 in EtOAc , AcOH , or EtOAc-NPhMe_2) of $(\text{CO}\cdot\text{CO}_2\text{Et})_2$ gives Et_2 *meso*-tartrate, m.p. 55°; the method is not practicable for making Et_2 *r*-tartrate. C_2D_2 is converted by O_3 in great dilution followed by atomised H_2O and steam into very pure glyoxal- d_2 , characterised as the *diphenylhydrazone*, $\text{C}_{14}\text{H}_{12.02}\text{D}_{1.98}\text{N}_4$, m.p. 170–171°. The further conversion into H sulphite, cyanohydrin, and *r*-tartaric acid is hampered by the poverty of the yields. $(\text{:C}\cdot\text{CO}_2\text{Me})_2$ in MeOH containing Pd-C is transformed by D_2 into a product with 1.7 D per mol., proving the exchange reaction ($\text{MeOH} + \text{D}_2 \rightleftharpoons \text{MeOD} + \text{HD}$) to have occurred to some extent in presence of the metal. The ester is therefore deuterated in presence of EtOAc and the product is treated with I for several hr. and then distilled, giving thereby Me_2 *trans*-ethylene- d_2 -dicarboxylate, $\text{C}_6\text{H}_{6.05}\text{D}_{1.97}\text{O}_4$, m.p. 105.5°, hydrolysed by boiling 0.2N- HNO_3 to the corresponding acid. This is oxidised by HClO_3 in presence of OsO_4 to *dl*- α - β -dihydroxyethane- d_2 - α - β -dicarboxylic acid, $\text{C}_4\text{H}_{4.05}\text{D}_{1.95}\text{O}_6$, m.p. 204–205° (NH_4H salt).

H. W.

Reducing action of ascorbic acid on mercuric chloride.—See A., 1939, I, 328.

Extent of the validity of the optical rotation rule in sugars. I. α -Methyl-*d*-arabonic acid. O. T. SCHMIDT and A. SIMON (J. pr. Chem., 1939, [ii], 152, 190–204).—3-Methylglucose [from glucose via diisopropylidenglucose and 3-methyldiisopropylidenglucose (improved preps.)] electrolysed in aq. CaBr_2 with CaCO_3 yields β -methylgluconic acid (I) [as *Ca* salt (II)], $[\alpha]_D^{20} -9.4^\circ \rightarrow +9.5^\circ$ in H_2O (2 days) [Na salt, $[\alpha]_D^{20} +15.6^\circ$ in H_2O ; *phenylhydrazide*, m.p. 140–141° (decomp.), $[\alpha]_D^{20} -1.7^\circ$ in H_2O]. Oxidation

of (II) with $\text{Fe}_2(\text{SO}_4)_3$, $\text{Ba}(\text{OAc})_2$, and H_2O_2 yields 2-methylarabinose (III), a syrup, converted by MeOH-HCl into 2-methylmethylarabinoside, b.p. 117–118°/0.1 mm., 165–168°/14 mm., $[\alpha]_D^{20} -15.4^\circ$ in H_2O , which with aq. H_2SO_4 regenerates (III), $[\alpha]_D^{20} -102^\circ$ in H_2O [p-toluenesulphonylhydrazide, m.p. 141°, $[\alpha]_D^{20} -16.8^\circ \rightarrow -20.6^\circ$ (3 days) in H_2O]. Oxidation of (II) with $\text{BaI}_2\text{-I-Ba}(\text{OH})_2$ in H_2O yields the lactone, m.p. 87°, $[\alpha]_D^{20} +52.7^\circ \rightarrow +47.4^\circ$ (90 hr.) in H_2O , of α -methyl-*d*-arabonic acid, (IV), $[\alpha]_D^{20} -35.5^\circ$ in H_2O [*phenylhydrazide*, m.p. 158–159° (decomp.), $[\alpha]_D^{20} -23.0^\circ$ in H_2O ; *amide*, m.p. 131°, $[\alpha]_D^{20} -53.2^\circ$ in H_2O ; *amide hydrate*, m.p. 96–97°, NH_4 salt, m.p. 146°, $[\alpha]_D^{20} -27.7^\circ$ in H_2O]. The $[\alpha]$ of (I), (IV), and their derivatives show that Hudson's rotation rule is not valid in these cases.

J. D. R.

Action of barium hydroxide on monobasic sugar acids. III. F. W. URSON, W. K. NOYCE, and W. D. ALBERT (J. Amer. Chem. Soc., 1939, 61, 779–786; cf. A., 1935, 327).—With 4N- $\text{Ba}(\text{OH})_2$ at 120° (24 hr.) *dl*-erythronic, *dl*-glucoheptonic, *dl*-rhamnohexonic, and *dl*-rhammonic acid give lactic acid 39.6, 32.5, 40.5, and 44.5, CO_2 a trace, 1.7, a trace, and 0.8, HCO_2H 8.8, 1.6, 1.7, and 6.6, AcOH 10.5, 5.5, 9.9, and 8.5, and $\text{H}_2\text{C}_2\text{O}_4$ 6.1, 6.2, 3.6%, and a trace, respectively. $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is unaffected. These and previous results are explained in the light of Schmidt's theory (A., 1935, 852), but are incompatible with fission at the ethylenic linking of the dienolic forms.

R. S. C.

Electrolytic preparation of glucuronic acid. R. A. LEUTGOEB and H. HEINRICH (J. Amer. Chem. Soc., 1939, 61, 870–873).—Cathodic oxidation of methylglucoside at high pressures (11 atm.) using pure Hg cathodes in an electrolyte of methylglucoside, Na_2SO_4 , and a trace of H_2SO_4 , yields methylglucuronide (20.2% yield). Various methods of obtaining the acid from the Me ester are given.

W. R. A.

Molecular structure of pectic acid. (A) G. H. BEAVEN and J. K. N. JONES. (B) F. SMITH (Chem. and Ind., 1939, 363, 363–364).—(A) Pectic acids from strawberry pectin and citrus pectin are similar and probably contain a chain of pyranose α -D-galacturonic acid residues (formula suggested). A partly degraded (HCl-MeOH) strawberry pectic acid is methylated (TIOEt-MeI) to a product, which resists hydrolysis but with HCl-MeOH under pressure gives methyl-2:3-dimethylgalacturonide Me ester (I) (mainly the furanose form), hydrolysed in H_2O to a dextrorotatory 2:3-dimethylgalacturonic acid (II) (pyranose form). With aq. Br this gives 2:3-dimethylmucic acid (III) (identified as Me ester γ -lactone), further oxidised (HIO_4) to $\text{CHO}\cdot\text{CO}_2\text{H}$ and d -[$\text{CH}(\text{OMe})\cdot\text{CO}_2\text{H}$] $_2$ (identified as amide).

(B) Degraded citrus pectic (pectolic) acid gives ($\text{Me}_2\text{SO}_4\text{-NaOH}$; $\text{Ag}_2\text{O-MeI}$) a product, hydrolysed by MeOH-HCl to (I), which with dil. H_2SO_4 gives (II) and thence (Br) (III), which gives the corresponding Me trimethoxy-ester, also obtained from methyl-2:3:5-trimethylgalactofuranoside (IV). Methylation of (II) gives a cryst. methyl-2:3:5-trimethylgalacturonide Me ester, also obtained from (IV) by KMnO_4 . Mol. wt. determinations indicate that the pectolic acid contains ≈ 12 units. 2:3-Dimethyl-

galacturonic acid and HCl-MeOH give the furanoside and not the pyranoside. R. S. C.

Polymethylenebisthionylacetic acids. E. LARSON (Svensk Kem. Tidskr., 1939, 51, 42—51).— $\text{SNa} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and $\text{Br} \cdot [\text{CH}_2]_n \cdot \text{Br}$ give *hexamethylenebis-sulphidoacetic acid*, m.p. 119°. Oxidation of the appropriate sulphido-acid with H_2O_2 - COMe_2 yields *mono-* (I), m.p. 156°, *tri-* (II), m.p. 118°, *tetra-*, m.p. 146°, *penta-*, m.p. 112°, and *hexa-*, m.p. 122°, *methylenebisthionylacetic acid*. There is no indication of optical isomerism. With warm dil. HCl the thionylacids yield $\text{SH} \cdot [\text{CH}_2]_n \cdot \text{SH}$ and $\text{CHO} \cdot \text{CO}_2\text{H}$ (isolated) which then cyclise to give $[\text{CH}_2]_2 \left\langle \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} \right\rangle \text{CH} \cdot \text{CO}_2\text{H}$ and

$\text{CO}_2\text{H} \cdot \text{CH} \left\langle \begin{smallmatrix} \text{S} \cdot [\text{CH}_2]_n \cdot \text{S} \\ \text{S} \cdot [\text{CH}_2]_n \cdot \text{S} \end{smallmatrix} \right\rangle \text{CH} \cdot \text{CO}_2\text{H}$ (III); e.g., (I) \rightarrow the acid (III) with $n = 1$, liquid, $(\text{CH}_2\text{SO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ \rightarrow the acid (III) with $n = 2$, m.p. 108°, and (II) \rightarrow the acid (III) with $n = 3$, liquid. M. H. M. A.

Preparation of α -hydroxyaldehydes. P. FRÉON (Ann. Chim., 1939, [xi], 11, 453—518).—Grignard's reagents behave normally with α -oximinoketones $\text{COR} \cdot \text{CR}'' \cdot \text{N} \cdot \text{OH}$ giving *tert.* alcohols, $\text{OH} \cdot \text{CRR}'' \cdot \text{CR}'' \cdot \text{N} \cdot \text{OH}$, hydrolysed to α -OH-ketones or α -OH-aldehydes. Compounds $\text{COR} \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ (I) undergo the following secondary reaction: (I) $\rightarrow \text{H}_2\text{O} + \text{R} \cdot \text{CO} \cdot \text{CN}$ (II); (II) + $\text{MgR}''\text{X} \rightarrow \text{CN} \cdot \text{CRR}'' \cdot \text{O} \cdot \text{MgX} \rightarrow \text{CN} \cdot \text{MgX} + \text{CORR}''$; this change is observed only when at least one of the radicals R and R'' is aliphatic. $\text{CHAc} \cdot \text{N} \cdot \text{OH}$ is best obtained by the gradual addition of H_2SO_4 to a solution of NaNO_2 and $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$ which has been in contact with KOH for 24 hr. Attempts to prepare AcCHO by the hydrolysis of $\text{CHAc} \cdot \text{N} \cdot \text{OH}$, $\text{CHAc} \cdot \text{N} \cdot \text{NH}_2$, or *methylglyoxal di-(K H sulphite)* give the compound in such dil. solution that its isolation is not practical. $\text{CMeAc} \cdot \text{N} \cdot \text{OH}$, best obtained by the action of EtNO_2 and HCl on COMeEt , is transformed by MgMeI into γ -oximino- β -hydroxy- β -methyl-*n*-butane, m.p. 87°, hydrolysed by boiling 10% $\text{H}_2\text{C}_2\text{O}_4$ to β -hydroxy- β -methylbutan- γ -one, b.p. 139—141° (semicarbazone, m.p. 164—165°). Similarly MgBuBr and $\text{CMeAc} \cdot \text{N} \cdot \text{OH}$ afford β -oximino- γ -hydroxy- γ -methyl-*n*-heptane, b.p. 101—102°/2.5 mm., hydrolysed to γ -hydroxy- γ -methylheptan- β -one, b.p. 84°/19 mm. (semicarbazone, m.p. 152°). $\text{CMeAc} \cdot \text{N} \cdot \text{OH}$ and Mg *n*-octyl bromide yield β -oximino- γ -hydroxy- γ -methylundecane, b.p. 154—155°/5 mm., m.p. ~ 8 —10°, hydrolysed by conc. HCl and 35% CH_2O to γ -hydroxy- γ -methylundecan- β -one (III), b.p. 118—120°/5 mm., and (?) γ -keto-8-methyldodecane- $\alpha\delta$ -diol, b.p. 176—178°/5 mm., which does not decolorize Br. (III) yields a semicarbazone, m.p. 130°, a non-cryst. *phenylurethane*, and an *acetate*, b.p. 130—133°/5 mm.; it is not dehydrated by $\text{H}_2\text{C}_2\text{O}_4$ at 130° or by boiling 25% H_2SO_4 . $\text{CMeAc} \cdot \text{N} \cdot \text{OH}$ and $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{MgBr}$ give β -oximino- γ -hydroxy- γ -*p*-tolyl-*n*-butane, m.p. 125—126°, hydrolysed by HCl and CH_2O to γ -hydroxy- γ -*p*-methylbutan- β -one, b.p. 116—117°/4 mm. (semicarbazone, m.p. 173°; *acetate*, b.p. 130—132°/4 mm., m.p. 47°, and its semicarbazone, m.p. 180°). $\text{CHAc} \cdot \text{N} \cdot \text{OH}$ and MgEtBr afford γ -methylpentan- γ -ol, b.p. 121—123°, COMeEt , and α -hydroxy- α -methylbutaldoxime, b.p. 95—96°/5 mm. It has not been

found possible to hydrolyse the oxime to monomeric α -hydroxy- α -methylbutaldehyde (IV). The only product isolated by the action of 10% $\text{H}_2\text{C}_2\text{O}_4$, 5% H_2SO_4 , or HCl is α -methylcrotonaldehyde (semicarbazone, m.p. 225°) arising from the dehydration of (IV). Hydrolysis in the presence of CH_2O yields the compound, $\text{OH} \cdot \text{CMeEt} \cdot \text{CHO} \cdot \text{CH}_2\text{O}$, b.p. 70.5°/4 mm., and a little (?) *dimeric* α -hydroxy- α -methylbutaldehyde, b.p. 112—113°/3 mm. Under similar conditions $\text{CHAc} \cdot \text{N} \cdot \text{OH}$ and MgBuBr afford COMeBu , b.p. 124—126° (semicarbazone, m.p. 116—117°), and α -hydroxy- α -methylhexaldoxime, b.p. 103—105°/2.5 mm., hydrolysed to α -methyl- Δ^a -hexenal (V), b.p. 72—74°/39 mm. (semicarbazone, m.p. 183—184°; *oxime*, b.p. 88—90°/5 mm.; *p*-nitrophenylhydrazone, m.p. 148—149°), and α -hydroxy- α -methylhexaldehyde, b.p. 86—88°/35 mm. (semicarbazone, m.p. 142—143°; non-cryst. *phenylhydrazone* and *phenylurethane*), dehydrated by anhyd. $\text{H}_2\text{C}_2\text{O}_4$ at 130° to (V) and converted by boiling Ac_2O into (V) and α -acetoxy- α -methylhexaldehyde, b.p. 96—98°/28 mm. (semicarbazone, m.p. 159—160°). $\text{CHAc} \cdot \text{N} \cdot \text{OH}$ and MgPhBr yield COPhMe , Ph_2 , and α -hydroxy- α -phenylpropaldoxime, b.p. 155—156°/5 mm., hydrolysed by $\text{HCl} \cdot \text{CH}_2\text{O}$ to α -hydroxy- α -phenylpropaldehyde, b.p. 101°/4 mm. (semicarbazone, m.p. 182—183°; *acetate*, b.p. 114—115°/2 mm.). $\text{CHBz} \cdot \text{N} \cdot \text{OH}$, obtained from COPhMe and EtNO_2 , is transformed by MgEtBr into COPhEt and α -hydroxy- α -phenylbutaldoxime, b.p. 157—158°/4 mm., hydrolysed (conc. $\text{HCl} \cdot \text{CH}_2\text{O}$) to α -hydroxy- α -phenylbutaldehyde, b.p. 108—111°/5 mm. (semicarbazone, m.p. 187—188°; *acetate*, b.p. 126—128°/8 mm.). $\text{CHBz} \cdot \text{N} \cdot \text{OH}$ is transformed by MgBuBr into a product, hydrolysed to α -hydroxy- α -phenylhexaldehyde, b.p. 124—126°/4 mm. (*oxime*, b.p. 162—163°/3 mm.; semicarbazone, m.p. 170—170.5°; *acetate*, b.p. 145—150°/9 mm.), which appears to polymerise somewhat rapidly. $\text{CHBz} \cdot \text{N} \cdot \text{OH}$ and MgPhBr afford diphenylglycollaldoxime, m.p. 122—123°, hydrolysed to a non-distillable liquid and a solid diphenylglycollaldehyde, m.p. 161—163°, each of which gives the same semicarbazone, m.p. 241—242° (decomp.), in almost theoretical yield. $\text{CHBz} \cdot \text{N} \cdot \text{OH}$ and $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{MgBr}$ yield *phenyl-p*-tolylglycollaldoxime, b.p. 204—209°/5 mm. (slight decomp.), hydrolysed by $\text{HCl} \cdot \text{CH}_2\text{O}$ to *phenyl-p*-tolylglycollaldehyde, b.p. 172—175°/4 mm. (slight decomp.) [semicarbazone, m.p. 232—233° (slight decomp.)]. H. W.

isoPropyrideneglyceraldehyde. VII. Preparation of *l*-glyceraldehyde and *l*-(—)-isopropylideneglycerol. E. BAER and H. O. L. FISCHER (J. Amer. Chem. Soc., 1939, 61, 761—765).—*l*-Mannono- γ -lactone, when first treated with CaCO_3 in hot H_2O and then hydrogenated in dil. H_2SO_4 at 80 atm. (3 days) in presence of PtO_2 and a little Fe_2O_3 , gives 66% of *l*-mannitol (I), m.p. 162—163°, α 0 (lævorotatory in aq. H_3BO_3) [trimethylene, m.p. 227°, $[\alpha]_D +106.2^\circ$ in CHCl_3 , triisopropylidene (II), m.p. 69—70°, $[\alpha]_D -12.6^\circ$ in abs. EtOH , and Ac_6 derivative, m.p. 121°, $[\alpha]_D -25.2^\circ$ in CHCl_3]. Reduction for 20 hr. only gives 30% of *l*-mannose. With COMe_2 - ZnCl_2 at room temp. (I) gives the $\alpha\beta\gamma$ -diisopropylidene derivative (56%), m.p. 122° [and some (II)], oxidised

by $\text{Pb}(\text{OAc})_4$ in C_6H_6 to *l*(-)-isopropylideneglycer-aldehyde (III) (73%), b.p. 40.5–41.5°/11 mm., $[\alpha]_D$ -5.61° in C_6H_6 . Hydrolysis then gives *l*(-)-glyceraldehyde (IV), a syrup, $[\alpha]_D$ -13.8° in H_2O (dimeron derivative, m.p. 198°, $[\alpha]_D$ -198° in dry EtOH; 2 : 4-dinitrophenylhydrazone, m.p. 147–148°). $[\alpha]$ of *l*- or *d*-(IV) falls to 7.8° in 8 days, but is restored to 14° by recrystallisation; possible causes of these changes are discussed. Hydrogenation (Ni) gives *l*(-)-isopropylideneglycerol, b.p. 72–72.5°/8 mm., $[\alpha]_D$ -13.4° (no solvent), -10.8° in C_6H_6 , +1.7° in H_2O .

R. S. C.

Influence of ketones on the Cannizzaro-Tischtschenko reaction. P. P. SURMIN (J. Gen. Chem. Russ., 1938, 8, 1390–1393).—The catalytic effect of ketones on the reaction $2\text{CH}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{MeOH}$ falls with increasing mol. wt. of the ketone, and with increasing temp. and $[\text{NaOH}]$, being in all cases negative when the $[\text{NaOH}]$ is > 10%. R. T.

Mechanism of formation of ketones from carboxylic acids. O. NEUNHOEFFER and P. PASCHKE (Ber., 1939, 72, [B], 919–929).—Evidence is adduced in favour of the hypothesis that the formation of ketones from acids and their salts is due to the intermediate production of β -CO-acid or its salt which subsequently undergoes decarboxylation: $\text{Ca}(\text{OAc})_2 \rightarrow \cdot\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Ca}\cdot\text{OH} \rightarrow \text{COMe}_2$. This is suggested by the failure of salts of acids in which CO_2H is united to *tert*-C [$\text{Bu}^t\text{CO}_2\text{H}$; $\text{CH}_2(\text{CMe}_2\cdot\text{CO}_2\text{H})_2$] to yield ketones. In the cases of phenylglycine-*o*-carboxylic acid and thiosalicyl-*S*-acetic acid the production of the CO-acid occurs at a temp. below that required for decarboxylation and the acids can therefore be isolated (this is not usually the case). The assumption that $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Ca}\cdot\text{OH}$ is an intermediate in the formation of COMe_2 from $\text{Ca}(\text{OAc})_2$ is in accord with the observed production of CaO and CO_2 and foreshadows the production of a neutral, enol carboxylate $\text{CMe} \left\langle \begin{smallmatrix} \text{CH}_2\text{CO} \\ \text{O} \end{smallmatrix} \right\rangle \text{Ca} \text{O}$ which cannot yield ketone without addition of H_2O or acid; this explains the observed increase in yield if steam is used or excess of acid is employed. At 430° Ba adipate which has been dried at 110° gives cyclopentanone (II) in 84% yield. If the salt has been desiccated in dry N_2 at 250° it gives at 430° (II) and cyclopentene (III); the residual BaCO_3 contains considerable amounts of C. If free adipic acid is added to (I) decomp. occurs extensively at 260° and the yield of (II) is somewhat > that obtained from the pure salt. An excess of basic components depresses the temp. of decomp. of (I) but encourages the by-products. In presence of BaO the main product is (III). Ba cyclopentanone-2-carboxylate (IV), the possible intermediate in the decomp. of (I), passes when heated into (III) and a carbonaceous residue. The Ca salt is decomposed more readily and the K salt is unstable at room temp. Although the isolation of (IV) as an intermediate in the decomp. of (I) is impossible, its formation is readily established analytically. Decomp. of $\text{o-CO}_2\text{Ba}_{0.5}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Ba}_{0.5}$ occurs at 410°, giving a product with a pronounced reaction with FeCl_3 which is more intense with the substance

obtained with NaOH-KOH at 220° or 280°; this when heated with H_2O yields hydrindone, establishing thus the intermediate production of the expected hydrindonecarboxylic acid. The presence of basic components is not necessary since Et H adipate affords Et cyclopentanone-2-carboxylate when slowly distilled. In Jena glass or SiO_2 vessels adipic acid is almost quantitatively transformed into (II) at 290° or 300° and β -*o*-carboxyphenylpropionic acid gives hydrindone; sebacic and azelaic acid yield cyclic ketones but the yield is as small as when their salts are used. Experiments in sealed tubes show that basic substances are very helpful if not essential for the production of COMe_2 from AcOH . In open tubes the losses appear considerably greater for some unexplained reason. The reversibility of the reaction is established by the production of min. amounts of AcOH from COMe_2 , steam, and CO_2 and of adipic acid from CO_2 , H_2O , and (II) at 330°. In the production of ketones from aromatic acids it appears that a CO-carboxylic acid is first produced by a type of Friedel-Crafts synthesis and this is subsequently decarboxylated. H. W.

Bromination of aliphatic ketones. S. V. SHAH and D. G. PISHAVIKAR (J. Univ. Bombay, 1938, 7, 178–183).—A detailed account of work already noted (A., 1939, II, 6). COMeEt and Ac_2 give Br_4 (not Br_2 -) and $\text{CO}(\text{C}_5\text{H}_{11})_2$ gives a Br_3 -derivative.

R. S. C.

Purification and criteria of purity of acetone. J. TIMMERMANS and L. GILLO (Rocz. Chem., 1938, 18, 812–829).— COMe_2 is purified by thrice-repeated fractional distillation over P_2O_5 ; the product, b.p. 56.20°/760 mm., d^{20}_D 0.81243, contains H_2O 0.0002, MeCHO < 0.0001, AcOH 0.0002, and CO_2 0.0008%.

R. T.

Oxidation of aldoses by hypoiodite. II. K. MYRBÄCK (Svensk Kem. Tidskr., 1939, 51, 74–84; cf. A., 1939, II, 142).—In the examination of the oxidation of aldoses by alkaline I solution and the parallel transformation of OI' into IO_3' it is found that the rate of reduction of OI' by glucose (I) is very great at the concn. of I and alkali customary in the Willstätter-Schudel determination. Under these conditions the production of OI' is extremely rapid and it is questionable whether the reduction of OI' by (I) takes place with sufficient rapidity to allow a trustworthy determination of OI' present. In more strongly alkaline solution the rates of oxidation of (I) and formation of IO_3' decrease greatly and the results are irregular. This effect is still more marked in aq. Na_2CO_3 or NaHCO_3 . IO_3' can be determined accurately if the change is stopped by the introduction of Na_3AsO_3 . The solution is treated with solid NaHCO_3 and H_2O and saturated with CO_2 , after which it is titrated with I in presence of starch. H. W.

Periodic acid oxidation of β -methyl-*D*-mannopyranoside. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 959–960).— β -Methyl-*D*-manno- and -*D*-galacto-pyranoside with HIO_4 , followed by $\text{Br-H}_2\text{O-BaCO}_3$, give *L'*-methoxy-*D*-hydroxymethyldiglycollic acid, in conformity with the accepted structures. R. S. C.

Esters of oses; azoyl [*p*-benzeneazobenzoyl] esters. W. S. REICH (Compt. rend., 1939, 208, 589—591).—*p*-Benzeneazobenzoic acid with SOCl_2 in boiling C_6H_6 affords *p*-benzeneazobenzoyl chloride (I) (azoyl chloride), m.p. 93°. Prolonged interaction of (I) with glucose in dry $\text{C}_5\text{H}_5\text{N}$ at 0° to -20° affords α -*d*-glucopyranose penta-*p*-benzeneazobenzoate, m.p. 234—236°, $[\alpha]_{\text{D}}^{20} +193^\circ$ in CHCl_3 . Fructose similarly affords β -*d*-fructopyranose penta-*p*-benzeneazobenzoate, m.p. 135—136°, $[\alpha]_{\text{D}}^{20} -345^\circ$ in CHCl_3 . J. L. D.

Separation of sugars by chromatography of their coloured esters. W. S. REICH (Compt. rend., 1939, 208, 748—749).—The separation of β -*d*-fructopyranose pentabenzeneazobenzoate, m.p. 135—136°, $[\alpha]_{\text{D}}^{20} -340^\circ$ in CHCl_3 , and α -*d*-glucopyranose pentabenzeneazobenzoate, m.p. 234—236°, $[\alpha]_{\text{D}}^{20} +197^\circ$ in CHCl_3 (preceding abstract), using columns of Al_2O_3 or SiO_2 , is detailed. A. J. E. W.

Walden inversion in the sugar group. II. Alkali-stability of the sulphonyl group in sulphonates of sugar derivatives. A. MÜLLER, M. MÓRICZ, and G. VERNER (Ber., 1939, 72, [B], 745—753).—Walden inversion during the removal of *p*- $\text{C}_6\text{H}_4\text{MeSO}_2$ and formation of anhydro-sugars from sugar *p*-toluenesulphonates appears to be connected with *trans*-dehydration. β -Glucose tetra-acetate 4-methanesulphonate is converted by successive treatments with HBr-AcOH at 15—20° and Ag_2CO_3 -abs. MeOH into β -methylglucoside triacetate 4-methanesulphonate, m.p. 110—111°, $[\alpha]_{\text{D}}^{21} -42.1^\circ$ in CHCl_3 , converted by NaOMe (1 mol.) in MeOH into 3:4-anhydro- β -methylgalactoside, (I), m.p. 158°, $[\alpha]_{\text{D}}^{21} -119.4^\circ$ in H_2O , and by <1 mol. of NaOMe into β -methylglucoside 4-methanesulphonate, m.p. 160°, transformed by further action of NaOMe into (I). β -Methylgalactoside and PhCHO at 150°/400 mm. afford 4:6-benzylidene- β -methylgalactoside, m.p. 199—200°, $[\alpha]_{\text{D}}^{20} -34.1^\circ$ in CHCl_3 , converted by Ac_2O and NaOAc at 100° into 4:6-benzylidene- β -methylgalactoside 2:3-diacetate, m.p. 155°, $[\alpha]_{\text{D}}^{20} +75.2^\circ$ in CHCl_3 . This is transformed (H_2 -Pd-C-EtOH) into β -methylgalactoside 2:3-diacetate (+0.5 H_2O) (II), m.p. 72—73°, $[\alpha]_{\text{D}}^{20} +2.8^\circ$ in CHCl_3 , converted by *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ in abs. $\text{C}_5\text{H}_5\text{N}$ at 15—20° into β -methylgalactoside 2:3-diacetate 4:6-di-*p*-toluenesulphonate, m.p. 152—153°, $[\alpha]_{\text{D}}^{22} +54.7^\circ$ in CHCl_3 , which is transformed by anhyd. NaI in dry COMe_2 at 140° into 6-iodo- β -methylgalactoside 2:3-diacetate 4-*p*-toluenesulphonate, m.p. 113—115°, $[\alpha]_{\text{D}}^{20} +40.2^\circ$ in CHCl_3 , unaffected by $\text{AcOH-Ac}_2\text{O-TIOAc}$ at 100°. $\text{C}_6\text{H}_5\text{Cl}$ and (II) in abs. $\text{C}_5\text{H}_5\text{N}$ at room temp. afford 6-triphenylmethyl- β -methylgalactoside 2:3-diacetate, m.p. 205—206°, $[\alpha]_{\text{D}}^{23} +2.1^\circ$ in CHCl_3 , in which the OH at $\text{C}_{(4)}$ could not be caused to react with *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$. 6-Triphenylmethyl- β -methylgalactoside 2:3-diacetate 4-methanesulphonate, m.p. 155—156°, $[\alpha]_{\text{D}}^{21} +21.0^\circ$ in CHCl_3 , is converted by AcBr in AcOH into β -methylgalactoside triacetate 4-methanesulphonate, m.p. 125—126°, $[\alpha]_{\text{D}}^{24} +6.2^\circ$ in CHCl_3 . This is unchanged by treatment with NaOMe (1 mol.) in MeOH followed by $\text{Ac}_2\text{O-NaOAc}$, yields β -methylgalactoside 4-methanesulphonate, m.p. 154—155°, when the solution is boiled, and gives dark brown, resinous products with a large excess of NaOMe. 4:6-Benzylidene- α -methylglucoside and

Ac_2O in anhyd. $\text{C}_5\text{H}_5\text{N}$ yield the 2:3-diacetate, m.p. 117—118°, $[\alpha]_{\text{D}}^{21} +198.0^\circ$ in CHCl_3 , whence α -methylgalactoside 2:3-diacetate, m.p. 100—101°, or (+1 H_2O), m.p. 81—82°, $[\alpha]_{\text{D}}^{20} +164.4^\circ$ in CHCl_3 . The anhyd. substance is transformed by *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ in anhyd. $\text{C}_5\text{H}_5\text{N}$ into α -methylgalactoside 2:3-diacetate 4:6-di-*p*-toluenesulphonate, m.p. 132°, $[\alpha]_{\text{D}}^{22} +106.6^\circ$ in CHCl_3 , and by $\text{C}_6\text{H}_5\text{Cl}$ in anhyd. $\text{C}_5\text{H}_5\text{N}$ at 40° into 6-triphenylmethyl- α -methylgalactoside 2:3-diacetate, m.p. 85—86°, $[\alpha]_{\text{D}}^{20} +175.6^\circ$, which could not be esterified at $\text{C}_{(4)}$ by *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$. H. W.

Ring structure in some derivatives of sorbose. R. L. WHISTLER (Iowa State Coll. J. Sci., 1938, 13, 97—99).—Oxidation of tetranethyl-*l*-sorbose (I) (cf. Arragon, A., 1936, 1234) with HNO_3 affords *d*-dimethoxysuccinic acid, so that (I) and α -methyl-*l*-sorbose (II) probably have pyranose structures. *l*-Sorbose (III) with dry EtOH-1% HCl affords α -ethyl-*l*-sorbo-pyranoside (IV), m.p. 116° $[\alpha]_{\text{D}}^{20} -73.9^\circ$ in H_2O [tetra-acetate, m.p. 75° $[\alpha]_{\text{D}}^{20} -54.6^\circ$ in CHCl_3 , identical with the compound obtained by ethylating sorbose 1:3:4:5-tetra-acetate (V); (V) has a pyranose ring because acetylation of (II) and methylation of (V) yield the same compound]. (II) and (IV) are formed and hydrolysed at equal rates. Equimol. amounts of (III) and CaCl_2 afford $\text{C}_6\text{H}_{12}\text{O}_6\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ (α -form), m.p. 159°, $[\alpha]_{\text{D}}^{20} -24.2^\circ$ to -23.9° in H_2O in 15 min., which when acetylated gives a penta- or tetra-acetate according to the conditions. *l*-Sorbose ethylthioacetal penta-acetate, prepared by Wolfrom and Thompson's method (A., 1934, 636), has b.p. 200°/vac., $[\alpha]_{\text{D}}^{20} -13.1^\circ$ in CHCl_3 and does not exhibit mutarotation. J. L. D.

Hydrogenation of saccharides. II. K. YOSHIKAWA and S. HANAI (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 1262—1277).—Hydrogenation of glucose (70—120°) and of sucrose and starch (160—180°) at 80—300 atm. with Ni or Ni-Fe catalysts yields mixtures of hexitols. At 190—240°, propylene glycol and glycerol are formed in good yields, together with $(\text{CH}_2\cdot\text{OH})_2$, EtOH, and MeOH. The mechanism of the hydrogenation is discussed. A. Li.

Tubasclepiadin. E. BUREŠ, M. ULRYCHOVÁ, and A. JINDRA (Rocz. Chem., 1938, 18, 404—410).—*Tubasclepiadin*, $\text{C}_{33}\text{H}_{71}\text{O}_{34}\cdot\text{CO}_2\text{H}$, decomp. 190°, prepared from *Asclepias tuberosa*, L., roots, yields 98.3% of glucose when hydrolysed with 6% HCl in EtOH. The aglucon, *tubasclepin*, $\text{C}_{23}\text{H}_{36}\text{O}(\text{OH})_6$, is isolated from the hydrolysate. R. T.

Pigments of cotton flowers. VII. Position of the glucose residue in gossypitrin. P. S. RAO and T. S. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 177—180; cf. A., 1937, II, 445).—Gradual addition of 20% NaOH and Me_2SO_4 to gossypitrin acetate in COMe_2 yields *hexamethylgossypitrin*, m.p. 290° (decomp.) after darkening, hydrolysed by 7% H_2SO_4 to 3:5:8:3':4'-pentamethylgossypetin, m.p. 252—254°. This is transformed by NaOAc and boiling Ac_2O into the acetate, m.p. 167—169°, converted by NaOH and Me_2SO_4 into 3:5:7:8:3':4'-hexamethylgossypetin, m.p. 170—172°. Gossypitrin is therefore the 7-glucoside of gossypetin. H. W.

Synthesis of tetradeca-acetylcrocine and related compounds. R. KUHN and Y. WANG (Ber., 1939, 72, [B], 871—878; cf. A., 1938, III, 763).—Ag₂ mesaconate is converted by acetobromoglucose (I) in anhyd. C₅H₅N in the dark and preferably with the avoidance of heating into *mesaconoyldi-(d-glucose 2:3:4:6-tetra-acetate)*, m.p. 198°, $[\alpha]_D^{25} -20.5$ in CHCl₃, converted by NH₃-abs. EtOH under very mild conditions into mesacondiamide, m.p. 176—177°, and by NaOMe (Zemplén) into pure *d-glucose*. The Ag₂ salt of *trans-crocetin* (II) is transformed by (I) in anhyd. C₅H₅N in absence of light into *trans-crocetin di-(β-d-glucose ester 2:3:4:6-tetra-acetate)*, m.p. 180—181°, $[\alpha]_D^{25} -59.0 \pm 0.0$ in CHCl₃, which is converted by NH₃ in abs. EtOH into *trans-crocetin di-β-d-glucose ester* in poor yield; its absorption bands in all examined solvents are identical with those of natural crocin, which it also resembles in its transformation in MeOH containing a little NaOH into *trans-crocetin Me₂ ester*. Crocin is transformed by Ac₂O in C₅H₅N into *crocine tetradeca-acetate* (III), m.p. 188—189° (corr.), $[\alpha]_D^{25} -54.5 \pm 0.0$ in CHCl₃ containing 1% of EtOH. (II) and α-acetobromogentiobiose in C₅H₅N give *trans-crocetin di(gentiobiose ester 2:3:4:2':3':4':6'-hepta-acetate)*, identical with (III) in m.p., $[\alpha]_D^{25}$, cryst. form, solubility, and absorption spectrum. Optical activity and synthesis indicate the great probability that in crocin both gentiobiose residues are in β-glucosidic union as esters with crocetin. The high optical activity, $[\alpha]_D^{25} -1760$ in H₂O, of crocin is very remarkable. H. W.

Synthesis of ruberythric acid, the main alkaloid of madder. G. ZEMPLÉN and R. BOGNÁR (Ber., 1939, 72, [B], 913—919).—Alizarin (I), 1-bromoglucose 2:3:4-triacetate, and Ag₂O in quinoline give 2-alizarin-β-glucoside 2':3':4'-triacetate (II), m.p. 234—236° after softening at 225°, converted by Ac₂O into 2-alizarin-β-glucoside penta-acetate, m.p. 199—200°, $[\alpha]_D^{25} -84.8$ in CHCl₃; (II) is too sparingly sol. in the usual media to be helpful in the synthesis of ruberythric acid (III). Gradual addition of aq. KOH to (I) and acetobromocellobiose in COMe₂ affords 2-alizarin-β-cellobioside hepta-acetate, m.p. 244—246° (corr.), transformed by Ac₂O-C₅H₅N into the octa-acetate, m.p. 224—225° (corr.), $[\alpha]_D^{25} -70.9$ in CHCl₃. Under similar conditions (I) and acetobromoprimverose give 2-alizarin-β-primveroside hepta-acetate, m.p. 231—232°, $[\alpha]_D^{25} -109.6$ in CHCl₃, hydrolysed to 2-alizarin-β-primveroside, m.p. 259—261°, identical with (III). H. W.

Polysaccharides. XXIX. Constitution of the dextran produced from sucrose by *Leuconostoc dextranicum*. S. PEAT, (Miss) E. SCHLÜCHTERER, and M. STACEY. XXX. Polysaccharide produced from sucrose by *Betabacterium vermiciforme* (Ward-Mayer). W. D. DAKER and M. STACEY (J.C.S., 1939, 581—585; 585—587).—XXIX. The dextran, $[\alpha]_D^{25} +180$ in H₂O, and Me₂SO₄-30% NaOH-COMe₂ (+ dioxan) at 40—50° (12 methylations) give a product, OMe 44—44.5%, $[\alpha]_D^{25} +210$ to $+214$ in CHCl₃, which is heated with 50% aq. AcOH containing 4% HCl until an equilibrium val. of $[\alpha]_D^{25} +58$ is reached. Me laevulate is removed by Ba(OH)₂. Conversion into methylglucosides indicates mainly

(90%) 2:3:4-trimethylglucopyranose (I) (corresponding anilide, m.p. 145—146°) (as the β-methylglucoside) and a little tetramethylglucose (II) (0.23%) (as tetramethylmethylglucoside), characterised by fractional crystallisation of the anilides. (I) is oxidised by HNO₃ (*d* 1.26) at 90—100° to trimethylsaccharic acid, and by Br at 40° to 2:3:4-trimethyl-δ-gluconolactone. The dextran is constituted on the same general plan as starch, cellulose, etc., i.e., a chain of *d*-glucopyranose units linked glucosidically with each other, but the linkings involve the terminal CH₂OH of each unit. The 1:6-glucosidic linking probably has the α-configuration (formula given). The yield of (II) corresponds with a max. chain length of 550 glucose units, compared with a min. of 200 by osmotic pressure measurements (cf. A., 1938, II, 310; Fairhead *et al.*, A., 1938, III, 699).

XXX. The dextran, $[\alpha]_D^{25} +180$ in H₂O, synthesised from sucrose by *Betabacterium vermiciforme* (Ward-Mayer) gives a homogeneous methylated product, OMe 44%, $[\alpha]_D^{25} +210$ in CHCl₃, hydrolysed by 50% AcOH-2% HCl on the bath (100°) to 2:3:4-trimethyl- (90%) and 2:3:4:5-tetramethyl-glucopyranose (5%). The particle of methylated dextran, measured by osmotic pressure methods, corresponds with a chain length of ~500 glucose units. The dextran is constituted of α-glucopyranose residues united by 1:6-glucosidic linkings. It differs from the dextran described previously (part XXIX) in that the basal chains consist of only 25 glucose units. A. T. P.

Constitution of cherry gum. I. Composition. J. K. N. JONES (J.C.S., 1939, 558—563).—Cherry gum resembles damson gum in properties (cf. Hirst and Jones, A., 1938, II, 394) and is converted into the acidic polysaccharide by pptn. with EtOH from an aq. HCl solution. It has equiv. wt. ~1450, $[\alpha]_D^{25} -28$, and it differs from the wild cherry-tree gum described by Butler *et al.* (A., 1932, 202). Analysis indicates 11.9% of uronic anhydride and 57% of pentosan. Graded hydrolysis with H₂O at 90—95° is recorded, and varying $[\alpha]_D$ and I vals. are observed. The sugar residues are combined: *l*-arabinose (I) (6 mols.), *d*-galactose (2 mols.), *d*-mannose (1 mol.), and *d*-glucuronic acid (1 mol.); the gum also contains a little *d*-xylose. The EtOH-insol. polysaccharide (II) from the hydrolysis contains the four last-named in proportions 2 mol., 1 mol., 1 mol., and ~3%. When boiled with *n*-H₂SO₄ for 4 hr., (II) also gives β-*d*-glycuroinosido-2-*d*-mannose, further treated as, and identical with, that from the damson gum. (I) appears to be combined in the furanose form, since its rate of hydrolysis is the same as that of the (I) in the damson gum mol. A. T. P.

Ageing of starch solutions.—See A., 1939, I, 258.

Ethers of starch. P. P. SCHORIGIN, N. N. MAKAROVA-ZENLIANSKAJA, R. L. BILENKO, V. A. DEREVITZKAJA, and V. T. SCHEMATEENKOVA (J. Gen. Chem. Russ., 1938, 8, 1910—1917).—Potato starch is soaked in 33% NaOH, and the product treated with excess of OH·CH₂·CH(OH)·CH₂Cl (I) or OH·CH(CH₂Cl)₂ (II) in COMe₂ (24 hr. at the b.p., under reflux), to yield products respectively sol. and insol. in H₂O or aq. NaOH; presence of small amounts

of (II) in (I) leads to formation of insol. products. The ethers obtained with (I) contain 1—3 glycerol residues per $C_6H_{10}O_5$ unit. *Acetates* of the glycerol ethers are described. The β -hydroxyethyl ether of starch (*triacetate*, *trinitrate*) is obtained with $(CH_3)_2O$, and the CH_2 ether (*acetate*) with CH_3SO_4 . R. T.

Carbohydrates. XI. Mode of reaction of cellulose with alkalis. T. LIESER, L. HENRICH, and F. FIGHTNER (*Annalen*, 1939, 538, 99—109; cf. A., 1938, I, 29).—Cotton linters is mercerised in 5N-NaOH, pressed, and washed with Pr^2OH until the washings are free from or contain a min., approx. const. amount of NaOH. The residue has the composition $2C_6H_{10}O_5 \cdot 3NaOH$. When similarly mercerised cellulose (I) is washed with *n*-alcohols the residue contains less NaOH. It appears that in alkali hydroxide of increasing concn. (I) unites additively with increasing amounts of NaOH. The change is due to the OH groups of the micelle surface which are available to NaOH. Alkali addition and hydrolysis of soda-cellulose are in equilibrium dependent on concn., temp., and type of (I). As expected, it is found that the amount of alkali hydroxide fixed by (I) decreases with increasing mol. vol. of the alkali (KOH, RbOH, CsOH) since the possible degree of penetration is lessened. It follows that the ratio of the main valency chains of the micelle surface to those of the micelle interior is not a fixed conception but is relative and dependent on the mol. vol. of the agent with which (I) reacts. The hypothesis explains the observations that the presence of neutral salts increases the amount of added alkali and that, other things being equal, more alkali is added at low than at high temp. The evidence now advanced favours the view that (I) and alkali yield additive compounds (II). The reactions of these compounds as alcoholates, e.g., in the formation of viscose, is explained by the assumption of an equilibrium almost entirely displaced towards (II). H. W.

Carbohydrates. XII. Mode of reaction of cellulose dissolved in copper oxide-ammonia. I. T. LIESER and H. SWIATKOWSKI (*Annalen*, 1939, 538, 110—119; cf. A., 1937, II, 480).—NaOH in increasing concn. is added to cellulose (I) dissolved in $Cu(OH)_2 \cdot NH_3$ saturated with $Cu(OH)_2$ and the ppt. is washed with alkali hydroxide until the filtrate is colourless. The dark blue product is washed with Pr^2OH until a min., practically const. amount of NaOH passes into the alcohol. After being washed with Et_2O and dried, the product shows variations in composition but analysis indicates a compound $(C_6H_{10}O_5)[C_6H_7O_2(OH)_3 \cdot 1.5Cu(OH)_2 \cdot 3NaOH]$. If Pr^2OH is replaced by $EtOH$ the results are more variable and less reproducible. Better results are obtained with $Ba(OH)_2$ and the product after being washed with MeOH conforms nearly to $(C_6H_{10}O_5)[C_6H_7O_2(OH)_3 \cdot 1.5Cu(OH)_2 \cdot 1.5Ba(OH)_2]$. Compounds of these compositions are obtained in a satisfactory and reproducible manner by the action of the requisite alkali hydroxide on cupricellulose $(C_6H_{10}O_5)[C_6H_7O_2(OH)_3 \cdot 1.5Cu(OH)_2]$. Since (I) which has been treated with $Cu(OH)_2$ and an org. base is converted by NaOH or $Ba(OH)_2$ into substances of the approx. composition

$[C_6H_7O_2(OH)_3 \cdot 1.5Cu(OH)_2][C_6H_7O_2(OH)_3 \cdot 3NaOH, 1.5Ca(OH)_2]$ and $[C_6H_7O_2(OH)_3 \cdot 1.5Cu(OH)_2][C_6H_7O_2(OH)_3 \cdot 1.5Ba(OH)_2 \cdot 1.5Cu(OH)_2]$, it follows that the alkali or alkaline-earth hydroxide is able to displace from its additive compound the $Cu(OH)_2$ which, on account of its insolubility, remains in the material. It appears therefore that even in the last described conditions NaOH or $Ba(OH)_2$ cannot penetrate into the interior of the micelle and by analogy that the action of NaOH or $Ba(OH)_2$ on micellar cupricellulose consists in expulsion of $Cu(OH)_2$ and formation of an additive compound with the OH groups of the main valency chains at the micelle surface. It is remarkable that a much less conc. alkali is required for reaction with cupricellulose than with normal (I). $Cu(OH)_2$ is not free in the products but its mode of union has not been elucidated. H. W.

Ethers of cellulose with glycerol. II. P. P. SCHORIGIN and J. A. RIMASCHEVSKAJA (*J. Gen. Chem. Russ.*, 1938, 8, 1903—1909).—The monoglyceryl ether obtained from cellulose and $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$ containing 1% of $OH \cdot CH(CH_2Cl)_2$ (I) is insol. in H_2O , and its acetates and nitrates are insol. in AcOH or $COMe_3$. This effect is ascribed to linking of adjacent cellulose chains by β -hydroxypropyl bridges formed from (I). Only relatively inconsiderable destruction of cellulose is involved in the reactions of formation of mono- and di-glyceryl ethers. R. T.

Kinetics of thermal decomposition of the methylamines.—See A., 1939, I, 326.

Reaction of α -methylhydroxylamine with organic compounds of magnesium and lithium, as a method of synthesis of primary amines. N. I. SCHEVERDINA and K. A. KOTSCHESCHKOV (*J. Gen. Chem. Russ.*, 1938, 8, 1825—1830).—The reactions $MgRX + NH_2 \cdot OMe \rightarrow NH_2R + MgX \cdot OMe$; $LiR + NH_2 \cdot OMe \rightarrow NH_2R + LiOMe$ are described ($R = Et, iso-C_5H_{11}, CHMeEt, Bu^v, Ph, p-C_6H_4Br$; $X = Cl, Br, I$). R. T.

Preparation and cyclisation of monoacyl-ethylenediamines. A. J. HILL and S. R. ASPINALL (*J. Amer. Chem. Soc.*, 1939, 61, 822—825).— $(CH_2 \cdot NH_2)_2$ and RCO_2Et at 100° give 50—85% of $COR \cdot NH \cdot [CH_2]_2 \cdot NH_2$ (A) and small amounts of $(CH_2 \cdot NH \cdot COR)_2$. If R is aliphatic, (A) are converted into 4:5-dihydroglyoxalines by dehydration by CaO at 225° , but if R is aromatic, ring-closure occurs on distillation alone at 200° ; the aroylamides are isolated from the primary reaction mixture only by solvent-extraction. The following are described. *N*-Acetyl-, m.p. 51° , b.p. $128^\circ/3$ mm. (*phenyl-carbamide*, m.p. 191° , and *thiocarbamide* derivative, m.p. 172° ; *picrate*, m.p. 175°), *N*-propionyl-, b.p. $130^\circ/3$ mm. (*picrate*, m.p. 148°); *phenyl-carbamide*, m.p. 180° , and *thiocarbamide* derivative, m.p. 143°), *N*-benzoyl-, an oil (*phenyl-carbamide*, m.p. 215° , and *thiocarbamide* derivative, m.p. 150°), and *N*-*p*-toluoyl-ethylenediamine [*β -acylaminoethylamines*], an oil (*phenyl-carbamide*, m.p. 191° , and *thiocarbamide* derivative, m.p. 173°), 2-Methyl-, m.p. 103° (lit. 105°), b.p. 197° (sublimes in vac.; lit. 195 — 198° , 198 — 200°) [*picrate*, m.p. 204° (lit. 205°)], 2-ethyl-, m.p. 48° (lit. 38°), b.p.

200°/760 mm., 90°/4 mm., 2-phenyl-, m.p. 101°, b.p. 162°/5 mm. [picrate, m.p. 244° (lit. 233°); phenyl-carbamide, m.p. 156°, and thiocarbamide derivative, m.p. 104°], and 2-p-tolyl-4:5-dihydroglyoxaline, m.p. 183°, sublines in vac. (picrate, m.p. 203°; phenylcarbamide derivative, m.p. 157°). NN'-Di-p-toluylethylenediamide, m.p. 244°. High temp. and deficiency of ester favour formation of (A) or dihydroglyoxaline at the expense of the diamide. M.p. are corr. R. S. C.

Preparation of putrescine from butadiene. W. LANGENBECK, W. WOLTERS DORF, and H. BLACHNITZKY (Ber., 1939, 72, [B], 671—672).—The liquid $\alpha\delta$ -dibromo- Δ^6 -butene greatly predominates if the substance is prepared in the dark and under these conditions it can be kept for months without appreciable change. In direct sunlight it passes very rapidly into the solid isomeride (I). $\text{o-C}_6\text{H}_4(\text{CO})_2\text{NK}$ in boiling MeOH transforms (I) into $\alpha\delta$ -diphthalimido- Δ^6 -butene, m.p. 226—227°, hydrogenated (PtO₂ in AcOH) to $\alpha\delta$ -diphthalimidobutane, m.p. 219°, which is hydrolysed by conc. HCl at 130° to putrescine hydrochloride. H. W.

Products of the hydrolysis of esters of choline. E. KAHANE and (MLLE.) G. ROUSSEAU (Bull. Soc. chim., 1939, [v], 6, 647—655; cf. A., 1937, II, 233).—Conditions for determining the presence of choline (I), neurine (II), or (NMe₃Cl·[CH₂]₂)₂O (III), are defined. Oxidation with excess of KMnO₄ in 5% H₂SO₄ at room temp. for 24 hr. shows that (I) absorbs 2 O with no formation of NMe₃, whilst (II) absorbs 5 O and affords 1 mol. of NMe₃. (III) is oxidised slowly and absorbs ~1 O, with formation of traces of NMe₃. The respective perchlorates of (I), (II), and (III) give similar results. Acid (aq. HCl) or alkaline (aq. NaOH) hydrolysis of the perchlorates of (I), (II), (III), palmityl-, benzoyl- (m.p. 200°), and chloroacetyl- (m.p. 97°)-choline, and of acetylcholine hydrochloride, affords (I). Acid hydrolysis of the perchlorates of chloro- and bromo-choline (IV) (m.p. 210°), and of the sulphuric ester, $\frac{[\text{CH}_2]_2\text{O}}{\text{NMe}_3} > \text{SO}_2$,

and nitric ester (V) (platinichloride, m.p. 227°) of choline, also gives (I). Alkaline hydrolysis, however, of the last four compounds [Na₂CO₃, Ba(OH)₂, KOH, or NaOH] affords (II). In a sealed tube, (IV) gives mainly (II) and some (I). The following preps. are recorded: diethylene glycol and SOCl₂ give a dichlorohydrin, b.p. 82—83°/23 mm., 1 mol. of which with 2 mols. of NMe₃ affords trimethyl- β -chloroethoxyethylammonium chloride, converted by NMe₃-EtOH at 100° into (III) (diperchlorate, m.p. >310°). (V) is prepared from the nitrate of (I) and HNO₃-AcOH-Ac₂O, or from (IV) and AgNO₃. A. T. P.

Hydroxyalkylhydrazines. (MLLE.) G. BENOIT (Bull. Soc. chim., 1939, [v], 6, 708—715).—(CH₂)₂O and the appropriate hydrazine afford: β -hydroxyethyl-, $\alpha\alpha$ -dimethyl- β - β' -hydroxyethyl-, b.p. 80°/32 mm. (picrate, m.p. 96°; dimethiodide), and $\alpha\alpha$ -diethyl- β - β' -hydroxyethyl-, b.p. 110—120°/35 mm. -hydrazine, with properties similar to those of NH₂-alcohols. $\alpha\beta$ -Oxido- β -methylbutane and 4 mols. of N₂H₄ at

100° afford β -methyl- β -hydroxybutyl-, b.p. 140—142°/50 mm., and similarly, $\alpha\alpha$ -dimethyl- β - β' -hydroxy- β' -methylbutyl-, b.p. 75°/24 mm., and $\alpha\alpha$ -diethyl-, b.p. 105°/26 mm., -hydrazine. Phenylethylene oxide, at 140°, gives β -hydroxy- β -phenylethyl-, b.p. 165°/4 mm. [with tetra-(β -hydroxy- β -phenylethyl)hydrazine, b.p. 215°/4 mm.], $\alpha\alpha$ -dimethyl-, b.p. 105°/5 mm., and -diethyl-, b.p. 120°/5 mm., 100°/1.6 mm., - β - β' -hydroxy- β' -phenylethyl-hydrazine. β -Phenyl- $\alpha\beta$ -propylene oxide gives β -hydroxy- β -phenylpropyl-, b.p. 185—190°/2.5 mm., $\alpha\alpha$ -dimethyl-, b.p. 100—105°/3.7 mm. (hydrochloride, m.p. 159°), and -diethyl-, b.p. 153—156°/3 mm., - β - β' -hydroxy- β' -phenylpropyl-hydrazine. α -Phenyl- $\alpha\beta$ -propylene oxide affords β -hydroxy- α -phenylpropyl-, b.p. 185—190°/20 mm., and $\alpha\alpha$ -dimethyl-, b.p. 110—112°/3.5 mm. (hydrochloride, m.p. 188—189°), and diethyl-, b.p. 130—135°/4 mm., - β - β' -hydroxy- α' -phenylpropylhydrazine (corresponding with isoephedrine). NMe₂NH₂ and CH₂Br·CH₂Bz in C₆H₆ give the α -methobromide of α -methyl- $\alpha\alpha'$ -benzoylthylhydrazine, m.p. ~200°, catalytically reduced (Pt) to (2 H₂) N-methyl-eephedrine, and (1 H₂) -ephedrone. $\alpha\alpha$ -Dimethyl- β -3:4-dihydroxybenzoylmethylhydrazine, however, is similarly reduced, with no loss of N, to the corresponding sec. alcohol, m.p. 96°, b.p. 205—207°.

A. T. P.

Urethanes as local anæsthetics. V. Alkyl γ -diethylaminopropylcarbamates. R. L. SHRINER and J. H. HICKEY (J. Amer. Chem. Soc., 1939, 61, 888—889; cf. A., 1938, II, 481).— γ -Diethylamino-propylphthalimide (prep. from the γ -Br-imide and hot NH₄Et₂), m.p. 144—145°, and aq. HCl at <25° give γ -diethylamino-n-propylamine, b.p. 167—170° (phenylcarbamide derivative, m.p. 116—116.5°), which with ClCO₂R, K₂CO₃, and a little H₂O in Et₂O gives Me, b.p. 125—127°/9 mm., Et, b.p. 138°/9 mm., Prⁿ, b.p. 147—149°/11 mm., Buⁿ, b.p. 158—161°/11 mm., Bu^t, b.p. 144—147°/8 mm., n-, b.p. 159—163°/9—10 mm., and iso-amyl, b.p. 139—143°/2 mm., and hexyl (I), b.p. 172—176°/10 mm., γ -diethylamino-n-propylcarbamate. These products are irritant and have varying anæsthetic power when injected (rabbit). Only (I) is active on the rabbit's eye. R. S. C.

Complex metallic compounds of optically active α -amino-acids. I. LIFSCHITZ and F. L. M. SCHOUTEDEN (Rec. trav. chim., 1939, 58, 411—422).—The prep. and polarimetric and photochemical properties of complex compounds, M[MX₂]_nH₂O (M = Cu, Ni, Zn, Cd, or Co), derived from *d*-glutamic and *L*-aspartic acids are described. No evidence for *cis-trans* isomerism was obtained. C. R. H.

α -Toluenesulphonyl-L-arginine, m.p. 256—257° (amide hydrochloride), and benzoyl-L-histidine-amide, m.p. 234°.—See A., 1939, III, 518.

New synthesis of octopine and its relationship to re-amination. F. KNOOP and C. MARTIUS (Z. physiol. Chem., 1939, 258, 238—242).—Hydrogenation (PtO₂) of arginine carbonate and AcCO₂H in H₂O yields octopine (I), decomp. 261°, [α]_D²⁰ +22.3° in H₂O; the reaction does not always proceed equally satisfactorily probably owing to the formation of a by-product which impedes the isolation of (I). Support is thus given to the hypotheses of re-amination

advanced by Herbst (A., 1935, 82) and Braunstein and Kritzmann (A., 1937, II, 448). H. W.

Utilisation of the optical isomerides of *NN'*-dimethylcystine. M. W. KIES, H. M. DYER, J. L. WOOD, and V. DU VIGNEAUD (J. Biol. Chem., 1939, 128, 207—216; cf. A., 1938, II, 434).—Methylation (MeI-NaOH), reduction, and benzylation (Na followed by CH_2PhCl in liquid NH_3) of di-*p*-toluenesulphonyl-*l*-cystine yields *S*-benzyl-*N*-methyl-*l*-cysteine, m.p. 207—208° (decomp.) (corr.), $[\alpha]_D^{25} +64.5^\circ$ in N-HCl , converted by Na-liquid NH_3 followed by I in Et_2O into *NN'*-dimethyl-*l*-cystine. This can be utilised for growth by rats in place of *l*-cystine (? by conversion into cystine via the keto-acid), but the *d*-isomeride cannot. A. Li.

Multivalent amino-acids and peptides. XI. Synthesis of diglycyl-*l*-cystine. J. P. GREENSTEIN (J. Biol. Chem., 1939, 128, 241—243).—Treatment of carbobenzyloxyglycine with PCl_5 in Et_2O , followed by *l*-cystine in aq. KOH, and reduction (Na in liquid NH_3) of the product, yields cryst. diglycyl-*l*-cystine ($+1\text{H}_2\text{O}$) (A., 1905, i, 30), m.p. 232°, $[\alpha]_D^{25} -108^\circ$ in N-HCl , rapidly hydrolysed by intestinal erepsin (the *l*-cystine produced being fully active), but not by carboxypepsidase. A. Li.

Capability of existence and stability of hydrazino-acids. H. BERGER (J. pr. Chem., 1939, [ii], 152, 267—328).— $\text{CET}_2\text{Br}\cdot\text{CO}_2\text{H}$ and N_2H_4 in H_2O yield $\text{OH}\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$ and $\text{CHMe}\cdot\text{CET}\cdot\text{CO}_2\text{H}$, whilst $\text{CET}_2\text{Br}\cdot\text{CO}_2\text{Et}$ gives *s*-di-(α -hydroxydiethylacet)hydrazide, m.p. 221° (decomp.), and *s*-di-(α -bromodiethylacet)hydrazide, m.p. 58—59°. $\text{CET}_2\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ with anhyd. HCN gives α -semicarbazidodiethylacetnitrile, m.p. 124—125°, which is hydrolysed by aq. acids to semicarbazide and by aq. alkalis to N_2H_4 ; with HCl in $\text{EtOH-Et}_2\text{O}$, semicarbazidodiethylacetic acid imidochloride, m.p. 110°, is formed. $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ and $\text{NH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ (I) yield α -hydrazinophenylacetic acid, but with $\text{NH}_2\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$ (I) does not yield the hydrazino-acid. $\text{CHEtBu}\cdot\text{CO}_2\text{H}$ (II) with P and Br yields α -ethylhexoyl bromide (III), b.p. 143°/31 mm., but this is not hydrolysed by H_2O to the free acid (IV). Attempts to prepare (IV) from (II) and Br do not succeed. Interaction of (III) and EtOH yields *Et* α -bromo- α -ethylhexoate, b.p. 114°/20 mm., which with N_2H_4 affords no hydrazino-compound. Treatment of $\text{CHBr}(\text{CO}_2\text{H})_2$, $\text{CHBr}(\text{CO}_2\text{Et})_2$, or $\text{CBu}^n\text{Br}(\text{CO}_2\text{H})_2$ [from $\text{CHBu}(\text{CO}_2\text{H})_2$ and Br in Et_2O] in EtOH or MeOH with N_2H_4 gives no hydrazino-acids, but α -bromohexoic acid gives α -hydrazinohexoic acid, m.p. 218° (decomp.) [*CHPh* derivative, m.p. 121° (decomp.)]. $\text{CPhBr}(\text{CO}_2\text{H})_2$ with N_2H_4 in EtOH gives α -hydrazinophenylacetic acid, whilst in H_2O the azine of phenylglyoxylic acid is formed. $\text{CPh}_2\text{Br}\cdot\text{CO}_2\text{H}$ and N_2H_4 in H_2O give α -hydrazinodiphenylacetic acid, m.p. 188° (decomp.) [(*CHPh*)₂ derivative, m.p. 172° (decomp.)]. α -Bromocyclohexylmalonic acid (V) and N_2H_4 in H_2O give α -hydrazinocyclohexylmalonic acid, m.p. 190° (decomp.) [*CHPh* derivative, m.p. 125°], whilst α -bromocyclohexylacetic acid, m.p. 92° [from (V), by heating], gives α -hydrazinocyclohexylacetic acid, m.p. 256° (decomp.) [*CHPh* derivative, m.p. 155° (decomp.)]. α -Bromohexahydrobenzylmalonic acid (VI),

m.p. 138° (decomp.) (from hexahydrobenzylmalonic acid and Br in Et_2O), with N_2H_4 gives α -hydrazinohexahydrobenzylmalonic acid, m.p. 122° (decomp.) [*CHPh* derivative, m.p. 82°], whilst α -bromo- β -cyclohexylpropionic acid, b.p. 176—180°/18 mm., m.p. 58° [from (VI), by heating], gives α -hydrazino- β -cyclohexylpropionic acid, m.p. 197—198° (decomp.) [*CHPh* derivative, m.p. 145—146° (decomp.)]. With N_2H_4 ($\text{OH})_2\text{C}(\text{CO}_2\text{Na})_2$ gives the Na_2 mesoxalate hydrazone, reduced (Na-Hg) to tartronic acid. ($\text{OH})_2\text{C}(\text{CO}_2\text{Et})_2$ and N_2H_4 in H_2O yield the hydrazone of mesoxalic acid dihydrazide, m.p. 165—170°, which with PhCHO gives benzylideneazine and a compound, $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_4$, m.p. 145—148°, and is hydrolysed by HCl to mesoxalic acid dihydrazide, m.p. 210—220°. $\text{CHPh}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ with N_2H_4 yields the N_2H_4 salt of diphenylpyruvic acid hydrazone, m.p. 137°, which with Na-Hg gives α -hydrazinodiphenylpropionic acid, m.p. 182—194° (decomp.) [*CHPh* derivative, m.p. 175° (decomp.)]. Similarly $\text{COBu}^n\cdot\text{CO}_2\text{H}$ with N_2H_4 gives the (N_2H_4)₂ salt, m.p. 143°, of $\text{H}_2\text{C}_2\text{O}_4$ and the N_2H_4 salt (VII) of trimethylpyruvic acid hydrazone, m.p. 185° (decomp.). This latter with aq. HCl gives the azine of trimethylpyruvic acid (VIII), m.p. 178° (decomp.), and on partial reduction (Na-Hg) gives the salt (IX), m.p. 146—147° (decomp.), of (VIII) with α -hydrazinotrimethylpropionic acid (X), m.p. 223—225° (decomp.) [*CHPh* derivative, m.p. 106°]. On hydrolysis (IX) gives a compound, $\text{C}_6\text{H}_{15}\text{O}_3\text{N}_2$ [*CHPh* derivative, m.p. 95°], which with NaOH gives (X). Reduction of (VII) with Na-Hg at 80° gives (X). J. D. R.

Organic catalysts for removal of carbon monoxide from formamide. T. ENKVIST [with, in part, P. TIKKANEN] (Ber., 1939, 72, [B], 878—884).—Pure $\text{HCO}\cdot\text{NH}_2$ in absence of catalyst does not evolve an appreciable amount of CO at 160.7° in 30 min. $\text{HCO}\cdot\text{NH}_4$, frequently present as an impurity in $\text{HCO}\cdot\text{NH}_2$, accelerates the change. Org. and inorg. acids, particularly H_2SO_4 , cause elimination of CO; reaction practically ceases at latest when a quantity of CO equiv. to the acid has been evolved. The action is apparently analogous to $\text{HCO}\cdot\text{NH}_2 + \text{HCl} = \text{NH}_4\text{Cl} + \text{CO}$. The usual NH_2 -acids do not accelerate the change appreciably. *N*-Acylated NH_2 -acids, including formamido-acids, as well as dibromotyrosine and 5-aminosalicylic acid at first accelerate the change considerably but the reaction soon ceases. The salts of certain *tert.* bases, in contrast to the corresponding free bases, greatly expedite the evolution of CO. The action is pronouncedly sp. Only salts of *tert.* bases with the $\text{C}_5\text{H}_5\text{N}$ ring, including the quinoline and isoquinoline group, are active beyond doubt but within this class the reaction is not universal. Me and other hydrocarbon residues appear to depress the activity, acting more powerfully when in the α - than in the β -position. α - NH_2 is strongly depressing. α -OH, β - NO_2 , and α - or β - CO_2H either are without influence or cause acceleration. With isoquinolinium chloride (I), H_2SO_4 , or hippuric acid (II) the rate of change declines very rapidly but attains a const. rate for a considerable time which is greater with (I) than with H_2SO_4 or (II). The action of (I) is purely catalytic. Addition of NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, or anhyd.

CaCl₂ to a mixture of (I) and HCO·NH₂ is without effect. The theory of the action is discussed.

H. W.

Higher aliphatic compounds. VII. The binary systems, palmitamide-stearamide, palmitanilide-stearanilide, and methyl palmitate-stearate. Purification of palmitic and stearic acid. J. B. GUY and J. C. SMITH (J.C.S., 1939, 615—618; cf. A., 1936, 822).—Purification, by distillation and crystallisation, of palmitic, m.p. 62·70°, f.p. 62·74°, and stearic acid, m.p. 69·62°, f.p. 69·60°, is described. Palmitamide, new m.p. 108·4°, and stearamide, new m.p. 105·3°, and the corresponding anilides, m.p. 90·6° and 95·05°, yield systems similar to those of the corresponding acids (*loc. cit.*), eutectic systems of solid solutions, 1:1 compounds being indicated by non-congruent m.p. Depressions of m.p. in the systems are < in the acid system and the m.p. of homologous amides lie closely together. Thus neither amide nor anilide is suitable for identifying a long-chain acid. Me palmitate, m.p. 29·55°, f.p. 29·35°, and stearate, m.p. 38·25°, f.p. 37·83°, are polymorphous, yielding transparent (metastable) and opaque crystals. In mixtures, the former is stabilised. The binary system yields inconclusive evidence on the compound formation between Me esters raised by X-ray measurements (Malkin, A., 1932, 326).

A. T. P.

Fulminate-ferricyanide reagent; colour reaction for fulminates. R. D. BARNARD (J. Lab. clin. Med., 1939, 24, 649—650).—Fulminates (Ag, Na, and Hg) give with Fe(CN)₆^{'''}, in neutral or alkaline solution, a characteristic deep rose colour. The titre of the fulminate-Fe(CN)₆^{'''} solution is equal to that of untreated Fe(CN)₆^{'''} solution as determined by titration of uric acid solutions.

C. J. C. B.

Preparation, stability, and physiological action of the heavy-metal salts of dithiocarbamic acids and thiol-acids. T. SCHINZEL and G. BENOFF (Bull. Soc. chim., 1939, [v], 6, 501—509).—The following diamines with CS₂ in Et₂O yield dithiocarbamic acids, [CH₂]_n·NR₂·NHEt₂·S>CS (R = H or Me) [having the m.p. (decomp.) given], which when mixed with metallic chlorides and then H₂O yield aq. solutions of the metal dithiocarbamate hydrochlorides: diethyl-β-amino-, 150° (Ag, Hg, Pb, and Cu salts), and -β-methylamino-ethylamine, 141—142° (Ag, Hg, Pb, and Cu salts); -γ-amino-, 150° (Ag salt), and -γ-methylamino-n-propylamine, 171—172° (Ag, Hg, Pb, and Cu salts); and -ω-methylamino-n-decylamine (from NEt₂·[CH₂]₁₀·OH and SOCl₂ followed by NH₂Me; b.p. 169—173°/16 mm.), 76° (Ag, Hg, and Cu salts); α-methylamino-γ-diethylamino-ββ-dimethyl-n-propane, 85—87° (Ag, Hg, and Cu salts); and δ-methylamino-β-diethylamino-n-hexane (from the Cl-compound and NH₂Me; b.p. 104°), 150—151° (Ag, Hg, and Cu salts). In stability, the metallic dithiocarbamates from *sec.-tert.* are > those from primary-*tert.* diamines, whilst Cu > Hg > Ag > Pb; excess of HCl usually accelerates the decomp. With CS(NH₂)₂, Et α-bromo-butyrate, -nonoate, -undecoate (from the acid chloride and Br, followed by EtOH; b.p. 155—163°) and -stearate yield 5-ethyl-, m.p. 196—198° (decomp.), -heptyl-, m.p. 191·5°, -nonyl-, m.p. 182·5°, and -hexa-

decyl-ψ-thiohydantoin, m.p. 174·5°, hydrolysed (EtOH-NaOH) to α-thiol-butyric, (Na-Hg, -Ag, -Cu, and -Pb salts very sol. in H₂O), -nonoic, m.p. 33° (Na-Hg salt sol., Na-Ag, -Cu, and -Pb salts insol. in H₂O), -undecoic, m.p. 49—50°, and -stearic acid, respectively. In all cases, the Cu^{II} salt decomposes in H₂O into the disulphide and the Cu^I salt, which reverts to the Cu^{II} salt in air. The toxicity of the salts of dithiocarbamic and thiol acids is >> that of the corresponding salts of mineral acids, and increases with increasing stability.

A. Lr.

Behaviour of some derivatives of azidoacetic ester towards potassium ethoxide. E. MÜLLER and W. STÖETZER (J. pr. Chem., 1939, [ii], 152, 219—236).—Azidoacetamide and KOEt in Et₂O yield CH₂N₃·C(OK):NH which with H₂O yields K azidoacetate and when heated evolves about 1 mol. of N₂ and 0·5 mol. of NH₃ and yields a substance, probably NH₂·CO·CH₂·N·N·CH₂·CO₂K. Azidoacethydrazide with KOEt in Et₂O evolves 1 mol. of N₂ and 1 mol. of NH₃, and yields the K₂ salt (I), decomp. 127°, of an acid, decomp. 215°, probably

$$\text{N} \begin{array}{c} \diagup \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \\ \diagdown \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \end{array} > \text{CO}, \text{ and acethydrazide}$$

(CHPh derivative, m.p. 136°). When hydrolysed with HCl, (I) yields CO₂, N₂H₄, NH₃, N₂, and HCN. Heated with NHPH·NH₂ in aq. AcOH, (I) yields glyoxylylhydrazide phenylhydrazone (II), m.p. 200° (decomp.), which with PhCHO yields benzylideneglyoxylylhydrazide phenylhydrazone, m.p. 229—230°. K carbomethoxymethylenehydrazinesulphonate with N₂H₄ gives an acid (III), (C₂H₅O₂N₂)₂, m.p. >250° [K (+1½H₂O), m.p. 119° (decomp.), and NH₄, m.p. >250°, salts], and glyoxylylhydrazide, m.p. 142—143° [identified as (II)]. The alkoxide of Et glyoxylate with N₂H₄ yields glyoxylylhydrazide hydrazone, m.p. 142—143° [(CHPh)₂ derivative, m.p. 215° (decomp.)], which with NHPH·NH₂ yields (II), and with HCl gives (III).

J. D. R.

Introduction of the azide group into complex salts. W. STRECKER and E. SCHWINN (J. pr. Chem., 1939, [ii], 152, 205—218).—The following complex salts are described: diammine Cu azide, [Cu(NH₃)₂]N₃ [from Cu(NH₃)₄SO₄ and NaN₃], tetrammine Cu azide, [Cu(NH₃)₄]N₃ [from CuN₃ and NH₃], tetrapyridine Cu azide, [Cu(C₅H₅N)₄]N₃ [from CuN₃ and C₅H₅N or from Cu(C₅H₅N)₄SO₄ and NaN₃], diethylenediamine Cu azide, [Cu en₂]N₃ [from Cu en₃SO₄ and BaN₃ or from (CH₂·NH₂)₂ and CuN₃], dipyridine Zn azide, [Zn(C₅H₅N)₂]N₃ [from Zn(C₅H₅N)₂Cl₂ and NaN₃], triethylenediamine Zn azide, [Zn en₃]N₃ [from Zn en₃Cl₂ and AgN₃], diammine Cd azide, [Cd(NH₃)₂]N₃ [from CdN₃ and NH₃], dipyridine Cd azide, [Cd(C₅H₅N)₂]N₃ [from Cd(C₅H₅N)₂Cl₂ and NaN₃], diethylenediamine Cd azide, [Cd en₂]N₃ [from Cd en₃Cl₂ and BaN₃], basic NH₄ Hg azide, Hg₂N₃ [from HgN₃ and NH₃], pyridine Hg azide, [Hg(C₅H₅N)]N₃ [from HgN₃ and C₅H₅N], hexammine Cr azide, [Cr(NH₃)₆]N₃ [from (NH₄)₆Cr₂(SO₄)₃ and BaN₃], chloropentammine Cr azide, [Cr(NH₃)₅Cl]N₃ [from (NH₃)₅ClCrSO₄ and BaN₃ or (NH₃)₅ClCrCl₂ and AgN₃], hexammine Ni azide, [Ni(C₅H₅N)₂]N₃ [from NaN₃ and (C₅H₅N)₄NiCl₂], hexapyridine Ni azide, [Ni(C₅H₅N)₆]N₃ [from Ni(C₅H₅N)₂N₃ and C₅H₅N or NiN₃ and C₅H₅N],

triethylenediamine Ni azide, $[\text{Ni en}_3]\text{N}_6$, [from NiN_6 and $(\text{CH}_3\text{NH}_2)_2$]. J. D. R.

Cd cacodylates.—See A., 1939, 1, 322.

Electrolysis of magnesium *n*- and *iso*-propyl bromide in ethyl ether. W. V. EVANS and D. BRAITHWAITE (J. Amer. Chem. Soc., 1939, 61, 898—900).—The products of electrolysis of MgEtI , MgMeBr , $\text{MgPr}^\alpha\text{Br}$, and $\text{MgPr}^\beta\text{Br}$ in Et_2O and of MgMeI in Bu_2O are in accord with the theory of Evans and Field (A., 1937, II, 10), but the following reactions also occur. PrOH is formed from MgPrBr by O_2 . Some O_2 and CO_2 are formed probably by discharge of $[\text{Et}_2\text{O.MgR}]^+$ with formation of Et_2O_2 , which then decomposes to (a) O_2 and (b) CO_2 , EtOH , CH_4 , and MeCHO . The tendency of the free radical to couple increases with the chain-length and decreases with chain-branching. R. S. C.

Action of secondary and tertiary magnesium-alkyl halides on esters and salts of acids. A. D. PETROV (Bull. Acad. Sci. U.R.S.S., Sér. Chim., 1938, 347—360).—The interaction of *Mg sec.* and *tert.* alkyl halides (MgXR) with esters ($\text{RCO}_2\text{R}'$) and salts (RCO_2M) of monobasic acids gives ketones COR_2 . Esters of the higher dibasic acids, however, give glycols $\text{OH}\cdot\text{CHR}'\cdot[\text{CH}_2]_n\cdot\text{CHR}'\cdot\text{OH}$. A scheme for the course of the reactions is given. S. H. H.

Organo-metallic compounds. IV. Tin alkyl compounds and their derivatives. T. HARADA (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 290—329; cf. A., 1925, i, 1254).— SnEt_4 [from Sn-Na-Zn (70 : 15 : 15) and EtBr] with 2 I yields SnEt_3I , and with 4 Br yields SnEt_2Br_2 , hydrolysed by Ag_2O in EtOH to $\text{SnEt}_2(\text{OH})_2$. $\text{SnEt}_3\cdot\text{OH}$ (from SnEt_3I and NaOH-EtOH) has a high mol. wt. in dry C_6H_6 , low in PhOH ; with P_2O_5 , or when distilled, it yields *Sn Et₃ oxide*, b.p. $154^\circ/10\text{ mm.}$, which with EtOH gives $\text{SnEt}_3\cdot\text{OH} + \text{SnEt}_3\cdot\text{OEt}$. Either oxide or hydroxide when boiled with H_2O yields $\text{SnEt}_3\cdot\text{OH}\cdot 0.5\text{H}_2\text{O}$, m.p. $125\text{--}143^\circ$. SnEt_2O (from SnEt_2Br_2 and aq. EtOH-NH_3) when distilled under reduced pressure yields $(\text{SnEt}_2)_2\text{O} + \text{SnO}_2$. SnEt_3Br or $\text{SnEt}_3\cdot\text{OH}$ with 1 Na in liquid NH_3 yields SnEt_3 , which is unimol. in dil., bimol. in conc., solution in C_{10}H_8 . SnEt_3 or SnEt_4 with Na in liquid NH_3 gives *Na triethylstannide*, which is rapidly oxidised by air, and with EtBr yields SnEt_4 . SnEt_2Br_2 with Na in liquid NH_3 gives successively SnEt_2 , *Na₂ tetraethyl-distannane*, and *Na₂ diethylstannide*. SnEt_2 is a white solid, decomp. $>150^\circ$, which with dil. HNO_3 gives a nitrate and H_2 , reduces AgNO_3 to Ag , reacts with halogens or Na , and when heated gives $(\text{SnEt}_2)_2 + \text{Sn}$; the mol. wt. of freshly prepared SnEt_2 in C_{10}H_8 is very high. Sn Et_3 halides with $\text{SnEt}_3\cdot\text{OH}$ in moist C_6H_6 give complex salts, $\text{SnEt}_3\text{X}\cdot 2\text{SnEt}_3\cdot\text{OH}\cdot\text{H}_2\text{O}$: *chloride*, m.p. 77° , *bromide*, m.p. 103° , and *iodide*, m.p. $108\text{--}110^\circ$. $\text{SnMe}_3\text{Cl}\cdot\text{SnMe}_3\cdot\text{OH}\cdot\text{H}_2\text{O}$, m.p. 90° (decomp.), similarly obtained, loses 1 H_2O over CaCl_2 . Sn Et_2 dihalides when boiled with SnEt_2O in moist C_6H_6 yield complex salts, $\text{H}[\text{O}\cdot\text{SnEt}_2]_3\cdot\text{OH}\cdot\text{SnEt}_2\text{X}_2$: *chloride*, m.p. $215\text{--}217^\circ$ (decomp.), *bromide*, m.p. $206\text{--}218^\circ$ (decomp.), and *iodide*, m.p. $205\text{--}213^\circ$ (decomp.), also produced when the Sn Et_3 halides are exposed to air in sunlight; P (A., II.)

the hot EtOH solutions of these on cooling yield salts $\text{Et}[\text{O}\cdot\text{SnEt}_2]_3\cdot\text{OEt}\cdot\text{SnEt}_2\text{X}_2$, m.p. $135\text{--}190^\circ$ (decomp.), $137\text{--}187^\circ$ (decomp.), and $137\text{--}198^\circ$ (decomp.), respectively. Sn Me_2 dihalides with excess of SnMe_2O yield in cold H_2O , $\text{H}[\text{O}\cdot\text{SnMe}_2]_3\cdot\text{OH}\cdot\text{SnMe}_2\text{X}_2$, in boiling EtOH , $\text{Et}[\text{O}\cdot\text{SnMe}_2]_3\cdot\text{OEt}\cdot\text{SnMe}_2\text{X}_2$ [bromide, m.p. $210\text{--}215^\circ$ (decomp.), iodide, m.p. $215\text{--}218^\circ$ (decomp.)], and in boiling H_2O , $[\text{SnMe}_2\text{O}]_2\cdot\text{SnMe}_2\text{X}_2$ (*chloride*); these compounds are sol. in H_2O , insol. in org. solvents. Mol. proportions of SnEt_2O and SnEt_2Br_2 in boiling C_6H_6 yield the *bromide*, $\text{SnEt}_2\text{O}\cdot\text{SnEt}_2\text{Br}_2$, insol. in H_2O and bi- or ter-mol. in C_6H_6 and C_{10}H_8 . SnEt_2O in dil. AcOH when neutralised with NaOH gives the *acetate*, $[\text{SnEt}_2\text{O}]_3\cdot\text{SnEt}_2(\text{OAc})_2$, (decomp. $>165^\circ$ to SnEt_2O), which has a high mol. wt. in C_{10}H_8 , low in PhOH . SnMe_2O under the same conditions gives the *acetate*, $\text{SnMe}_2\text{O}\cdot\text{SnMe}_2(\text{OAc})_2$, m.p. 231° . A. LI.

Organic compounds of titanium. V. M. PLETZ (J. Gen. Chem. Russ., 1938, 8, 1298—1301).— LiBu^α and $\text{TiCl}(\text{OEt})_3$ or $\text{TiCl}_2(\text{OEt})_2$ in C_6H_6 yield highly unstable $\text{TiBu}^\alpha(\text{OEt})_3$ or $\text{TiBu}^\alpha_2(\text{OEt})_2$ (not isolated). R. T.

Complex compounds of diguanide with ter-valent metals. V. Thiocyanates of chromium diguanides. P. RAY and H. SAHA (J. Indian Chem. Soc., 1938, 15, 633—638; cf. A., 1938, II, 435).— Cr triguanide hydroxide and excess of aq. NH_4SCN give a mixed ppt., a second crop of a *hydroxodithiocyanate*, $[\text{CrR}_3](\text{OH})(\text{SCN})_2$, where $\text{R} = \text{NH}[\text{C}(\text{NH})\cdot\text{NH}_2]_2$, and, after keeping for a few days (or when the initial reagents are heated until all free NH_3 is lost), the *bisdiguanide trithiocyanate* (I), $[\text{CrR}_2(\text{SCN})_2]\text{SCN}$. Cryoscopic and conductivity measurements show that in H_2O this forms $[\text{CrR}_2(\text{SCN})(\text{H}_2\text{O})](\text{SCN})_2$ and $[\text{CrR}_2(\text{H}_2\text{O})_2](\text{SCN})_3$. With AgNO_3 , (I) forms the *diaquotrinirate*, $[\text{CrR}_2(\text{H}_2\text{O})_2](\text{NO}_3)_3\cdot\text{H}_2\text{O}$ ($3\text{H}_2\text{O}$ lost at $120\text{--}125^\circ$). $[\text{CrR}_3]_2(\text{SO}_4)_3$ and $\text{Ba}(\text{SCN})_2$ give the *normal trithiocyanate*, $[\text{CrR}_3](\text{SCN})_3$, with a *hydroxoquoquibisdiguanide thiocyanate*, $[\text{CrR}_2(\text{OH})(\text{H}_2\text{O})](\text{SCN})_2$. E. W. W.

Werner complexes. Cobaltammines from optically active α -amino-acids. J. P. MATHIEU (Bull. Soc. chim., 1939, [v], 6, 873—882; cf. A., 1938, I, 122, 453).— $\text{NH}_2\cdot\text{R}\cdot\text{CO}_2\text{H}$, in feebly acid or neutral solution, and $\text{Br}_2[\text{Co en}(\text{OH}\cdot\text{OH}_2)](\text{cis})$, give complexes of type $\text{Br}_2[\text{Co en}(\text{CO}_2\text{R})]_2$ in 40—70% yield (similar absorption spectra; max. $485\text{--}490\text{ m}\mu$). The complexes can exist in two diastereoisomeric forms, separable by the differing solubilities of their *d*-bromocamphorsulphonates (A) or *d*-tartrates. Thus, glycine gives $\text{Cl}_2[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{N})] + \text{H}_2\text{O}$, and from the less sol. (A), $\text{I}_2[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{N})] + \text{H}_2\text{O}$ (cf. Meisenheimer, A., 1924, i, 1035). Alanine, $[\alpha]_{546} +2.4^\circ$ in H_2O , gives a Br_2 complex, $[\text{M}]_D -195^\circ$, and thence $\text{I}_2[\text{Co en}_2(\text{C}_3\text{H}_6\text{O}_2\text{N})] + 2\text{H}_2\text{O}$, $[\text{M}]_D +1300^\circ$; phenylalanine, $[\alpha]_D -33.7^\circ$ in H_2O , affords $\text{Br}_2[\text{Co en}(\text{C}_9\text{H}_{10}\text{O}_2\text{N})] + \text{traces of H}_2\text{O}$, $[\text{M}]_D -335^\circ$, and from the less sol. (A), a Br_2 complex, $[\text{M}]_D -2150^\circ$; valine, $[\alpha]_D +5.5^\circ$ in H_2O , gives a racemic Br_2 complex, and the less sol. (A) gives $\text{Br}_2[\text{Co en}_2(\text{C}_5\text{H}_{10}\text{O}_2\text{N})]$, $[\text{M}]_D +1000^\circ$. Leucine, $[\alpha]_D -10.7^\circ$ in H_2O , gives a racemic complex, $[\text{M}]_D -350^\circ$,

and from the less sol. *d*-tartrate, a bromide, $[M]_D +1900^\circ$; isoleucine, $[\alpha]_D +12^\circ$ in H_2O , gives a complex $[M]_D -560^\circ$. A comparative study of the optical activities of the complexes before and after resolving shows that the rotatory power of the former is due to relation of active NH_2 -acid and central chromophore atom, and not to a partial asymmetric synthesis. There is no apparent relation between the solubilities of (A) and the sign of the Cotton effect of the derived complexes.

A. T. P.

Constitution, optical activity, and photochemical behaviour of platinum complexes.

IV. I. LIFSCHITZ and W. FROENTJES (Z. anorg. Chem., 1939, 241, 134—144; cf. A., 1935, 1335; 1937, I, 285, 423).—Various criticisms of the author's work, and particularly those of Jensen (A., 1936, 410), are dealt with. Further experimental details of the resolution of $SEt\cdot CHMe\cdot CO_2H$ are given. By the action of $Br\cdot H_2O$ on *cis*- and *trans*- $[(SEt\cdot CHMe\cdot CO_2)_2Pt]$ the compounds *cis*- and *trans*- $[(SEt\cdot CHMe\cdot CO_2)_2PtBr_2]$, m.p. 105° and 165° , respectively, have been obtained. These differ from the compounds of the same formula described previously. They have strong oxidising properties, and their mol. rotations are at first of the same sign as those of the free acid, but rapidly change to the opposite sign and then more slowly return towards the original vals., the oxidising properties gradually disappearing. They are probably additive compounds containing mol. Br, and gradually change over into the previously-described compounds. The compounds $[X_2Pt(SRR')]$ described by Wardlaw *et al.* (A., 1930, 349) are probably of a similar character.

F. J. G.

Complex compounds of platinum metals with thio-, seleno-, and telluro-ethers. II. Influence of medium on formation of *cis*- and *trans*-isomerides.—See A., 1939, I, 334.

Dehydrogenation with selenium in the study of constitution of organic compounds. K. KRATZL (Österr. Chem.-Ztg., 1939, 42, 163—174).—A lecture.

Hydrogenation under high pressures of hydrogen of (A) cyclohexane, (B) methylcyclohexane. P. V. PUTSCHKOV and A. F. NIKOLAEVA. (C) Benzene. P. V. PUTSCHKOV. (D) Toluene, (E) hexahydromesitylene. P. V. PUTSCHKOV and A. F. NIKOLAEVA (J. Gen. Chem. Russ., 1938, 8, 1153—1158, 1159—1166, 1676—1681, 1756—1762, 1939—1942).—(A) Hydrogenation at $400^\circ/150$ atm. (MoS_2 catalyst) leads to methylcyclopentane (I) and *n*- and *iso*-hexane; at 500° unsaturated and aromatic hydrocarbons are also formed.

(B) The products obtained similarly from methylcyclohexane (II) were 1:2- (III) and 1:3-dimethyl- (IV), and ethylcyclopentane, together with branched-chain hydrocarbons.

(C) The chief product was (I), with cyclohexane and traces of *n*-hexane.

(D) At 400° the products were (III), (IV), and (II), whilst at 470° C_6H_6 and paraffin hydrocarbons were also obtained.

(E) The chief products were gaseous hydrocarbons. The liquid products included *n*-pentane and other

aliphatic hydrocarbons, together with cyclopentane derivatives.

R. T.

High-temperature hydrogenation of aromatic hydrocarbons. VIII. Condensation of cyclohexane in the process of hydrogenation of benzene. E. I. PROKOPETZ, A. N. FILARETOV, and V. A. PITSCHEKO. IX. Isomerisation of cyclohexane and methylcyclopentane. E. I. PROKOPETZ and A. N. FILARETOV (J. Appl. Chem. Russ., 1938, 11, 1626—1631, 1631—1635).—VIII. The yield of products of b.p. $>82^\circ$ obtained by hydrogenation of C_6H_6 (MoS_2 -Co catalyst) falls as the temp. is raised from 270° to 360° . These products are probably methylcyclohexane or dimethylcyclopentane, and dimethylcyclohexyl derivatives.

IX. The change cyclohexane \rightarrow methylcyclopentane is activated by MoS_2 -Co hydrogenation catalyst, which also catalyses the reaction of methylation of cyclic hydrocarbons.

R. T.

Thermo-polymerisation of cyclohexene.—See A., 1939, I, 326.

Catalytic transformations of 1-vinyl- Δ^3 -cyclohexene and 1-acetylenyl- Δ^1 -cyclohexene. R. J. LEVINA and S. J. LEVINA (J. Gen. Chem. Russ., 1938, 8, 1776—1779; cf. A., 1939, II, 205).—1-Vinyl- Δ^3 -cyclohexene passed over Pt-C at 200 — 205° in CO_2 yields PhEt and ethylcyclohexane. 1-Acetylenyl- Δ^1 -cyclohexene similarly gives only PhEt.

R. T.

Catalytic hydrogenation of compounds with several double linkings. Hydrogenation of diphenylfulvene. B. A. KAZANSKI and G. T. TATEVOSIAN (J. Gen. Chem. Russ., 1938, 8, 1428—1437).—Diphenylfulvene hydrogenated at room temp. (Pd and Pt catalysts in EtOH) yields successively diphenylcyclopentylidenemethane (I), m.p. 62.5 — 63° , and benzhydrylcyclopentane. (I) is also obtained from Et cyclopentanecarboxylate and $MgPhBr$.

R. T.

Aliphatic chloro-derivatives. XV. Action of quinoline on polyhalogeno-compounds. Dimethylenecyclohexene. D. V. TISCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 1326—1329).—1:1:2-Trichlorocyclohexane (I) heated with quinoline yields 1:2-dichloro- Δ^1 -cyclohexene, m.p. 26 — 27° , from which HCl is eliminated similarly, affording 2-chloro- Δ^1 :3-cyclohexadiene (II), b.p. 141 — 142° . 1-Chloro- Δ^1 -cyclohexene and Cl_2 yield (I) and 1:2-dichloro- Δ^2 -cyclohexene, b.p. 81.2 — $81.5^\circ/14$ mm., which with $CaCO_3$ in H_2O at 100° gives 2-chloro- Δ^2 -cyclohexen-1-ol, b.p. 84.5 — $85^\circ/11$ mm. (compound with $PhNCO$, m.p. 83 — 83.5°), dehydrated by passing over $MgSO_4$ at 270° to (II).

R. T.

Condensation of alcohols with aromatic compounds in presence of aluminium chloride. VI. Alkylation of halogen-substituted aromatic hydrocarbons with alcohols. I. P. TZUKERVANIK. IX. Condensation of 2-methylcyclohexanol, menthol, and borneol with benzene and toluene. I. P. TZUKERVANIK and N. G. SIDOROVA (J. Gen. Chem. Russ., 1938, 8, 1512—1515, 1899—1902).—VI. Alcohols and $PhCl$ heated at 100° with $AlCl_3$ yield *p*- $C_6H_4R\cdot Cl$ ($R = Bu^v$, *tert*- C_4H_9 , Pr^i , Et , *sec*-butyl, b.p. 212 — 214°). *o*- C_6H_4MeCl similarly yields

2-chloro-*tert*.-butyltoluene, b.p. 225—230°/730 mm., and 1-C₁₀H₇Cl gives 1-chloro-isopropyl-, b.p. 310—312°, and *tert*.-amyl-naphthalene, b.p. 305—310°.

IX. Cyclic alcohols and aromatic hydrocarbons are condensed in presence of AlCl₃ at 100°. 2-Methylcyclohexanol and C₆H₆ give methylcyclohexylbenzene, b.p. 142—143°/36 mm., and a mixture of *m*- and *p*-di(methylcyclohexyl)benzene; with PhMe a mixture, b.p. 152—154°/32 mm., of *m*- and *p*-methylcyclohexyltoluene was obtained. Menthol gives menthylbenzene with C₆H₆, and a mixture, b.p. 183—188°/50 mm., of *m*- and *p*-menthyltoluene with PhMe. Borneol reacts similarly to menthol. R. T.

Reactions of ferric chloride. I. M. DANGIAN (J. Gen. Chem. Russ., 1938, 8, 1780—1783).—PhMe and anhyd. FeCl₃ (90 min. at the b.p.) yield *p*-C₆H₄MeCl. Esters (EtOAc, EtOBz) react as follows: R·CO₂Et + FeCl₃ → R·CO₂·FeCl₂ + EtCl. EtOH and FeCl₃ give EtCl and FeCl₂·OH. PhOMe and FeCl₃ afford 4 : 4'-dimethoxydiphenyl. R. T.

Alkylation of aromatic hydrocarbons and their halogen derivatives by olefines and their halogen derivatives in presence of sulphuric acid as catalyst. R. TRUFFAULT (Bull. Soc. chim., 1939, [v], 6, 726—736).—Mainly an account of work previously abstracted (A., 1936, 832; 1938, II, 476). CH₂:CH·CH₂Cl, PhMe, and H₂SO₄ afford *p*-C₆H₄Me·CHMe·CH₂Cl, b.p. 105°/16 mm., whilst C₆H₆, CH₂:CH·CH₂Br, and H₂SO₄ give CHPhMe·CH₂Br. The phenylthiocarbamate of CHPhMe·CH₂·OH has m.p. 71° (cf. lit.). A. T. P.

Relative reactivities of organometallic compounds. XXV. Coupling reaction with halides of group VIII metals. H. GILMAN and M. LICHTENWALTER (J. Amer. Chem. Soc., 1939, 61, 957—959; cf. A., 1939, II, 233).—Conversion of MgArHal into Ar₂ by metals depends on formation of unstable compounds, MAr, MAr₂, etc., and the yield is a measure of the instability of the compounds. The following yields of Ph₂ are obtained from MgPhI in Et₂O-C₆H₆ by the salts named: PdCl₂, FeCl₂, CoBr₂ 98; NiBr₂ 100; RuCl₃ 99; RhCl₃ 97.5; OsCl₃ 53; IrCl₃ 28; PtCl₄ 6%. 2 : 4 : 6-C₆H₃Me₃·MgBr and CoBr₂ give 20% of dimesityl. In Et₂O, MgPhBr and Ni(CN)₂ give very slowly 27—30% of Ph₂. R. S. C.

Structure of polychlorodiphenyls. J. S. SALKIND and M. V. BELKOVA (J. Gen. Chem. Russ., 1938, 8, 1918—1921).—Ph₂ and Cl₂ at 90—200° (in presence of Fe) yield 2 : 4 : 5 : 3' : 4'-pentachloro-, b.p. 195—220°/10 mm., and 2 : 3 : 4 : 5 : 2' : 4' : 5'-heptachloro-diphenyl, b.p. 240—280°/20 mm., oxidised (HNO₃) to 2 : 4 : 5-trichloro- and 2 : 3 : 4 : 5-tetrachloro-benzoic acid, m.p. 190.5—191.5° (lit. m.p. 186°) (amide, m.p. 200—202°), respectively. R. T.

Properties and preparation of phenylallene. J. I. GINZBURG (J. Gen. Chem. Russ., 1938, 8, 1029—1041).—CHPh·CCl·CHO is reduced (activated Al) to α -chlorocinnamyl alcohol, b.p. 121.5—123.5°/1.5—2 mm., which with SOCl₂ in NPhMe₂ yields β -dichloro- α -phenyl- Δ^2 -propene, b.p. 109—111°/4—5 mm. This heated at 65—70° with Zn in EtOH and N₂ yields phenylallene (I), b.p. 69.5—71.5°/15 mm. (gives a

dimeride when kept), together with β -chloro- α -phenyl- Δ^2 -propene, b.p. 61.5—62.5°/2 mm. (I) heated with KOH in EtOH (6.5 hr. at 105—110°) gives CPh:CMc; this is not formed in the reaction between (I) and NaNH₂. R. T.

β -Diphenyl- Δ^2 -butadiene. C. H. F. ALLEN, C. G. ELIOT, and A. BELL (Canad. J. Res., 1939, 17, B, 75—88).— β -Diphenylbutadiene (I), conveniently prepared from (CPhMe·OH)₂ and AcBr in presence of a trace of β -C₁₀H₇·NHPh, is purified through its dibromide, m.p. 145—147°, which is shown to be the $\alpha\delta$ -derivative (cf. Stobbe, A., 1910, i, 235). Addition of HBr in CHCl₃-ascaridole (trace) or β -C₁₀H₇·NHPh affords α -bromo- β -diphenyl- Δ^2 -butene, m.p. 78°, converted by Zn dust in COMe₂ into 2-phenyl-3-methylindene. Reduction (H₂, PtO₂, EtOH) of (I) yields *meso*- β -diphenylbutane, m.p. 122° [also obtained (Wurtz synthesis) from CHPhMeBr], and (probably) the *dl*-form. N₂O₄ and (I) in cold C₆H₁₄ give $\alpha\delta$ -dinitro- β -diphenyl- Δ^2 -butene (II), m.p. 151°, and the $\gamma\delta$ -dinitro- Δ^2 -isomeride, m.p. 192°. The Na₂ salt of (I) with Br gives $\alpha\delta$ -dinitro- β -diphenyl- Δ^2 -butadiene, m.p. 184° (decomp.). Maleic anhydride and (I) in boiling C₆H₆ lead to *cis*-4 : 5-diphenyl- Δ^4 -tetrahydrophthalic acid, m.p. 193°, converted by KOH at 310° into the *trans*-acid, m.p. 228°, and *o*-C₆H₄Ph₂. Dehydrogenation (S at 200° in N₂) then gives 3 : 4-diphenylphthalic acid, m.p. 205—206° (decomp.) (anhydride, m.p. 102°), also obtained in poor yield from 3 : 4-diphenylfuran and (:CH·CO)₂O in AcOH-HBr and from (I) and (:C·CO₂Et)₂ at 180—190°. α -Naphthaquinone and (I) give 2 : 3-diphenyltetrahydroanthraquinone, m.p. 175—176°, dehydrogenated (air in EtOH-KOH) to 2 : 3-diphenylantraquinone (III), m.p. 211—212°. *p*-O:C₆H₄:O and (I) yield 6 : 7-7-diphenyl-5 : 8 : 9 : 10-tetrahydro-1 : 4-naphthaquinone, m.p. 163°. 2 : 4 : 1-(NO₂)₂C₆H₃·N₂·SO₃H (prep. with NO·SO₃H-C₆H₅N) with NH₂·SO₃H and (I) (in C₆H₅N) give a compound, ? C₂₂H₁₆O₄N₄, m.p. 166—168°, decomp. ~230°. Fusion of (III) with moist KOH at 250° affords *o*-C₆H₄Ph₂, BzOH, and 3 : 4-diphenylbenzoic acid, m.p. 218°. Br and *cis*-(IV) and *trans*-(CPhMe)₂ in CHCl₃ give β -dibromo- β -diphenylbutanes, m.p. 142—144° (decomp.) and 149—152°, respectively; debromination (Zn dust, COMe₂) gives (IV); Beschke's (I) (A., 1912, i, 839) is thus (IV). F. R. S.

Destructive chlorination of organic compounds. I. Naphthalene. V. I. SCHVEMBERGER [with V. M. GORDON] (J. Gen. Chem. Russ., 1938, 8, 1353—1360).—C₁₀H₈ and Cl₂ at 200—250° yield decachlorohydrindene and CCl₄; C₁₀Cl₈ is an intermediate. R. T.

Sulphonation. I. Mechanism of the process of monosulphonation. A. A. SRISKOV (J. Gen. Chem. Russ., 1938, 8, 1857—1863).—In presence of excess of C₁₀H₈ the system H₂SO₄-H₂O-C₁₀H₈, at 100°, consists of 3 layers, viz., unaltered C₁₀H₈, sulphonation products, and aq. H₂SO₄. With time the system becomes homogeneous, and represents a solution of C₁₀H₈ and H₂SO₄ in aq. C₁₀H₇·SO₃H. C₁₀H₈ is not sulphonated by 60% H₂SO₄, in which it is insol.; addition of anhyd. C₁₀H₇·SO₃H allows sulphonation to be effected by 44% H₂SO₄. The

action of $C_{10}H_7SO_3H$ is ascribed to binding of H_2O , and to homogenisation of the system. R. T.

Nitration by means of nitrogen peroxide. III. Aromatic hydrocarbons. P. P. SCHORIGIN and A. V. TOPTSCHIEV (J. Gen. Chem. Russ., 1938, 8, 981—985).—The following products are obtained from the appropriate hydrocarbons and N_2O_4 : 1- $C_{10}H_7NO_2$, at 18—20°, and also 1:5- and 1:8- $C_{10}H_6(NO_2)_2$, and 1:3:8- $C_{10}H_5(NO_2)_3$, at higher temp.; 2- and 4-nitrodiphenyl (18°); 9-nitro- and mainly 9:10-dinitro-anthracene (0—20°); 2- (mainly), 3-, 4-, and 9-nitrophenanthrene (0°). C_6H_6 or $C_{10}H_8$ with 10% N_2O_4 gives $PhNO_2$ or 1- $C_{10}H_7NO_2$, in theoretical yield. R. T.

Catalytic transformations of the dimeride of $\Delta^{1:3}$ -cyclohexadiene. B. A. KAZANSKI and L. G. VOLFSOON (J. Gen. Chem. Russ., 1938, 8, 1685—1690).—1:4-endoEthylene- $\Delta^{2:7}$ -hexahydronaphthalene in EtOH is hydrogenated (Pd catalyst) to the Δ^7H_8 -derivative, b.p. 113—114°/20 mm., dehydrogenated (C-Pt catalyst at 150°) to the 1:2:3:4- H_4 -derivative, m.p. 63.5°; at 350° $C_{10}H_8$ is produced. R. T.

Anthracene derivatives. III. Synthesis of anthracene-2:9:10-trisulphonic acid. B. P. FEDOROV and E. I. SCHELUDIAKOVA (J. Gen. Chem. Russ., 1938, 8, 1699—1703).—9:10-Dichloroanthracene-2-sulphonic acid and aq. Na_2SO_3 (25—30 hr. at 170—180°) yield anthracene-2:9:10-trisulphonic acid (I) (Na salt, +2 H_2O ; benzidine salt), together with anthrone-2-sulphonic acid. (I) yields anthracene-2-sulphonic acid when heated with aq. H_2SO_4 . R. T.

Synthesis of 2:6:8:12-tetraphenyl-5:11-di- p -diphenylnaphthacene and its photo-oxide. D. DUVEEN and A. WILLEMART (Bull. Soc. chim., 1939, [v], 6, 702—708).—Mainly abstracted previously (A., 1939, II, 55). γ -Phenyl- α -di- p -diphenylpropargyl alcohol or chloride (*loc. cit.*), on refluxing with H_2SO_4 -EtOH or EtOH, respectively, affords α -benzoyl- $\beta\beta$ -(di- p -diphenyl)ethylene, m.p. 162—163°. A. T. P.

Dehydration of hydroxy-compounds by pyrolysis of their potassium sulphate esters: cholesterylene and camphene. S. NATELSON and S. P. GOTTFRIED (J. Amer. Chem. Soc., 1939, 61, 971—972).—Cholesterol (I) and $SO_3-C_5H_5N-Ac_2O-C_6H_5$ followed by aq. KOH give *K cholesteryl sulphate*, m.p. 212° (decomp.), converted at 100° into cholesterylene and by very dil. H_2SO_4 at 100° into (I). *K bornyl sulphate*, m.p. 220° (decomp.), when heated at 200°, gives camphene. R. S. C.

9-Methyl-1:2:5:6-dibenzanthracene. L. F. FIESER and G. W. KILMER (J. Amer. Chem. Soc., 1939, 61, 862—865).—1- $C_{10}H_7-MgBr$ and 1:2- $C_{10}H_6(CO)_2O$ give 2- α -naphthoyl-1-naphthoic acid (I), m.p. (anhyd.) 183.5—184° or (+ $x C_6H_6$) ~120° (resolidifies) (lactol acetate, m.p. 179.5—181°), and smaller amounts of 1- α -naphthoyl-2-naphthoic acid, m.p. 244—245° (lactol acetate, m.p. 197.5—198.5°). Zn-NaOH converts (I) into tars. H_2-Cu chromite at 150—180°/80—140 atm. reduces (I), but only a little of the lactone (II), m.p. 170.5—171°, of 2- α -hydroxy-1'-naphthylmethyl-1-naphthoic acid and some

2- α -naphthylmethyl-1-naphthoic acid, m.p. 193—194° [also obtained from (II) by Zn-Hg-HCl or Zn-NaOH], are obtained. $MgMeI$ and (I) in C_6H_6 give the lactone (78%), m.p. 194.5—195°, of 2- α -hydroxy- α -1'-naphthylethyl-1-naphthoic acid, reduced by Zn-Hg-HCl-AcOH-PhMe to 2- α -1'-naphthylethyl-1-naphthoic acid, m.p. 221—222°. $ZnCl_2-Ac_2O-AcOH$ then yields 9-methyl-1:2:5:6-dibenz-10-anthrone (III) (94%), m.p. 203.5—204.5° (with $Ac_2O-C_5H_5N$ gives 9-methyl-1:2:5:6-dibenz-10-anthranyl acetate, m.p. 192—192.5°), reduced by Zn dust in NaOH-PhMe to 9-methyl-9:10-dihydro-1:2:5:6-dibenz-10-anthranol, m.p. 215—220° (soft glass, <200° (Pyrex), which with a little HCl in EtOH gives 9-methyl-1:2:5:6-dibenzanthracene, m.p. 192—194.5° [*picrate*, m.p. 186—186.5°; $C_6H_3(NO_2)_3$ derivative, m.p. 178.5—179°]. M.p. are corr. R. S. C.

Rearrangements of tetra-aryldiallenes. XII. Synthesis of 2:8-diphenylchrysene. C. S. MARVEL and W. J. PEPPEL (J. Amer. Chem. Soc., 1939, 61, 895—897; cf. A., 1938, II, 136).—*trans*-2:8-Diketo-1:2:6b:7:8:12b-hexahydrochrysene and $MgPhBr$ give a diol, dehydrated by hot AcOH to 2:8-diphenyl-6b:12b-dihydrochrysene (I), m.p. 265—266°, which with Se at 275—300° gives 2:8-diphenylchrysene (II), m.p. 285° (corr.). The absorption spectra of (I) and (II) do not resemble those of the hydrocarbons *A* and *B*, $C_{38}H_{38}$ (A., 1932, 50, 505). That of *B* resembles that of its precursor, $(C_6H_5)_2C:C(Ph)_2$, but has max. at higher λ . *B* may thus be derived by formation of one unsaturated ring. R. S. C.

Hydrofluoric acid as a condensing agent. I. W. S. CALCOTT, J. M. TINKER, and V. WEINMAYR (J. Amer. Chem. Soc., 1939, 61, 949—951).—Anhyd. HF at approx. room temp. causes a double "benzanthrone" synthesis with acetaldehyde and suitable cyclic compounds. Thus, 9-hydroxy-1:10-trimethylenepheneanthrene or phenanthrene gives mixed hydrogenated products, dehydrogenated, best by Hg, to perylene. 9:10-Dihydroanthracene gives 4:5-benzopyrene. α - and β - $C_{10}H_7OH$ give *perinaphthindone*. Acenaphthene gives a mixture. Higher condensation products are usually obtained also. R. S. C.

d - and l - β -p-Hydroxyphenylisopropylmethylamines.—See B., 1939, 551.

High-pressure hydrogenation of aniline.—See B., 1939, 463.

Antispasmodics. III, IV. F. F. BLICKE and F. B. ZIENTY (J. Amer. Chem. Soc., 1939, 61, 771—773, 774—776; cf. A., 1939, II, 106).—The following are prepared. The bases marked * are strong and those marked † are weak antispasmodics; *S* = stimulant. The bases not marked are substantially inactive. Figures in parentheses are m.p. of the hydrochlorides.

III. 2-, b.p. 74—76°/10 mm., and 3-Methylcyclohexylmethyl, b.p. 71—73°/7 mm., β -3-, b.p. 79—81°/5 mm., and β -4-methylcyclohexylethyl bromide, b.p. 78—79°/8 mm., are prepared from the alcohol by PBr_3 , and α -cyclohexylethyl bromide, b.p. 94—96°/26 mm., by $HBr-C_6H_6$. Methyl-hexyl-, b.p. 140—

142°/735 mm. (178—179°), β -ethylbutyl-, b.p. 128—129°/742 mm. (201—202°), β -ethylhexyl-, b.p. 73—75°/15 mm. (185—186°), α -octyl-, b.p. 78—79°/14 mm. (180—181°), α -methyl-n-heptyl-, b.p. 70—71°/14 mm., dihexyl-, b.p. 121—122°/19 mm. (144—145°), di- β -ethylbutyl-, b.p. 100—101°/13 mm. (154—155°), di- β -ethylhexyl-, b.p. 113—114°/6 mm. (aurichloride, m.p. 103—104°), dioctyl-, b.p. 136—138°/5 mm. (149—150°), di- β -hydroxyethyl- (S), b.p. 141—142°/18 mm., di- β -chloroethyl- [113—114° (lit. 116—117°)], di- β -N-morpholyethyl-, b.p. 161—164°/8 mm. (trihydrochloride, m.p. 277—278°), cyclohexylmethyl-2-furfuryl-, b.p. 103—105°/5 mm. (107—108°), β -cyclohexylethyl-2-furfuryl-, b.p. 121—123°/5 mm. (163—164°), 2-methylcyclohexylmethyl-, b.p. 57—61°/7 mm. (230—231°), 3-methylcyclohexylmethyl-, b.p. 58—60°/6 mm. (182—184°), β -3-methylcyclohexylethyl-, b.p. 74—75°/8 mm. (162—163°), β -4-methylcyclohexylethyl-, b.p. 81—82°/9 mm. (162—163°), di-2-methylcyclohexylmethyl- \dagger (188—189°), di-3-methylcyclohexylmethyl-, b.p. 135—140°/7 mm. (205—206°), di- β -3-methylcyclohexylethyl-, b.p. 158—161°/7 mm. (228—229°), and di- β -4-methylcyclohexylethyl-, b.p. 166—170°/9 mm. (241—242°), amine. β -cyclopentylethyl-ethyl-, b.p. 73—74°/13 mm. (197—198°), propyl-, b.p. 72—74°/5 mm. (251—253°), butyl-, b.p. 106—107°/13 mm. (278—279°), and amylamine, b.p. 98—100°/4 mm. (284—285°). N-Butyl- (S), b.p. 67—68°/10 mm. (213—214°), N-cyclohexyl- (S), b.p. 111—112°/12 mm. (254—255°), and N- β -cyclohexylethyl-morpholine (S), b.p. 132—134°/12 mm. (260—261°). Di- β -cyclopentylethyl-ethyl-, b.p. 140—145°/7 mm. (115—116°), propyl-, b.p. 147—150°/7 mm. (aurichloride, m.p. 145—146°), butyl-, b.p. 153—158°/6 mm. (aurichloride, m.p. 133—134°), and amylamine*, b.p. 163—168°/5 mm. Dicyclohexyl- \dagger [326—327° (cf. lit.)], and β -cyclohexylethyl- γ -cyclohexylpropyl-, b.p. 150—156°/6 mm. (322—323°), amine. NN'-Di- β -cyclohexylethylpiperazine \dagger (dihydrochloride, m.p. 325—326°). N- β -cyclohexylethyl- (S), b.p. 115—120°/8 mm. [dihydrochloride, m.p. ~305° (decomp.)], NN'-di- β -cyclohexylethyl-, b.p. 195—200°/8 mm. (dihydrochloride, m.p. 319—320°), and NN'-di- β -cyclohexylethyl-NN'-dimethyl-, b.p. 180—182°/9 mm. (dihydrochloride, m.p. 276—277°), ethylenediamine. NN'-Di- β -cyclohexyl-NN'-dimethyltrimethylenediamine*, b.p. 190—195°/5 mm. (dihydrochloride, m.p. 294—295°). Di- β -phenylethylethyl-, b.p. 176—178°/7 mm. [136—137° (lit. 134° and 137°)], propyl-, b.p. 170—172°/6 mm. (158—159°), and butylamine \dagger , b.p. 194—195°/9 mm. (140—141°). cycloHexylmethyl- β -cyclohexylethylamine*, b.p. 146—149°/5 mm. (116—117°). β -cycloHexylethyl- β -phenylethyl-ethyl-, b.p. 163—168°/7 mm. (117—118°), and butylamine \dagger , b.p. 180—182°/6 mm. (128—129°).

IV. Dibenzyl- (S), b.p. 161—162°/12 mm. (200—201°), dicinnamyl-, b.p. 180—185°/5 mm. (148—149°), di- γ -phenylpropyl-, b.p. 182—184°/6 mm. (aurichloride, m.p. 127—128°), di- δ -phenylbutyl-, b.p. 193—195°/6 mm. (aurichloride, m.p. 113—114°), and di-2-ketocyclohexylmethyl-methylamine \dagger , m.p. 170—172° [195—197° (decomp.)]. Benzyl-, b.p. 175—180°/10 mm. (141—142°), γ -phenoxypropyl-, b.p. 195—198°/4 mm. (130—131°), cyclohexylmethyl-,

b.p. 166—169°/9 mm. (185—186°), β -cyclohexylethyl-, b.p. 175—180°/8 mm. (211—212°), and β -cyclopentylethyl-cinnamylmethylamine \dagger , b.p. 164—167°/8 mm. (183—184°). cycloHexyl- β -cyclohexylethyl-, b.p. 133—137°/6 mm. (201—202°), and δ -cyclohexylbutyl-methylamine*, b.p. 151—155°/4 mm. (184—185°). cycloHexylmethyl- β -cyclohexylethyl-, b.p. 144—146°/6 mm. (250—251°), γ -cyclohexylpropyl-, b.p. 140—145°/6 mm. (199—200°), and δ -cyclohexylbutyl-methylamine*, b.p. 154—157°/6 mm. (179—180°). β -cycloHexylethyl-hexyl-, b.p. 113—117°/5 mm. (203—204°), octyl-, b.p. 139—141°/5 mm. (170—171°), benzyl-, b.p. 140—142°/4 mm. (242—243°), β -phenylethyl-, b.p. 150—152°/4 mm. (205—206°), γ -phenoxypropyl-, b.p. 168—171°/5 mm. (142—143°), β -cyclopentylethyl-, b.p. 137—139°/6 mm. (251—252°), 2-methylcyclohexylmethyl-, b.p. 137—139°/5 mm. (230—231°), γ -cyclohexylpropyl-, b.p. 153—156°/6 mm. (228—229°), δ -cyclohexylbutyl-, b.p. 160—165°/4 mm. (191—192°), and α -dimethyl- Δ^5 -hexenyl-methylamine \dagger , b.p. 140—145°/5 mm. Methyl- β -hydroxyethyl- β' - β' -cyclohexylethoxyethylamine \dagger , b.p. 142—143°/5 mm. R. S. C.

Nickel, cadmium, and lead sulphides as catalysts in the vapour-phase reduction of nitrobenzene.—See B., 1939, 463.

Exchange of chlorine substituted in aromatic nuclei for the amino-group. III. Kinetics of catalytic reaction of chlorobenzene with aqueous ammonia. IV. Kinetics of reaction of *p*-chloronitrobenzene with aqueous ammonia. N. N. VOROSHOV, jun., and V. A. KOBELEV (J. Gen. Chem. Russ., 1938, 8, 1106—1119, 1330—1335).—II. The velocity of the reaction $\text{PhCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Ph} + \text{HCl}$, at 180—220°, α concn. of PhCl and of catalysts (CuCl , CuBr , CuCl_2), but not to that of NH_3 . Where increase in $[\text{NH}_3]$ accelerates the reaction this is due to presence of undissolved PhCl ; the effect of increasing the $[\text{NH}_3]$ is thus to increase the effective $[\text{PhCl}]$. The reaction is retarded by NH_4Cl , to an extent $\propto [\text{NH}_4\text{Cl}]$. The velocity coeff., $\log k = 6.484 - 3606/T$ with CuCl , and $12.52 - 6520/T$, with CuCl_2 .

IV. The velocity of the reaction $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2 + \text{NH}_3 \rightarrow p\text{-NH}_2\text{C}_6\text{H}_4\cdot\text{NO}_2 + \text{HCl}$ is α concn. of substrates, and to the temp. ($\log k = 7.24 - 4681/T$). In presence of CuCl_2 catalyst the velocity also $\propto [\text{CuCl}_2]$.

R. T.

Preparation of dinitroanilines. E. MACCIOTTA (Annali Chim. Appl., 1939, 29, 81—82).—*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ (200 g.) is dissolved in HNO_3 -free HNO_3 (*d* 1.52; 500 c.c.) at 0° and slowly poured with stirring into a mixture of H_2SO_4 (500 c.c.) and AcOH (100 c.c.) at 0°. The solids separating on mixing with ice are fractionally crystallised from $\text{C}_6\text{H}_6\text{-COMe}_2$ (2 : 1), yielding 2 : 3- (95 g.) and 3 : 6- (NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NHAc}$ (20 g.). The residue from the mother-liquor with AcCl affords the 2 : 3- (5 g.), 3 : 6- (6 g.), and 3 : 4-isomeride (60 g.). F. O. H.

Orientation problems. II. Nitration of acetotoluides. A. MCGOOKIN and S. R. SWIFT (J.S.C.I., 1939, 58, 152—154).—Difficulties in drying $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ account for the high yields sometimes claimed (lit.). *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ (25 g.) added

with rapid stirring to HNO_3 (d 1.52; 50.84 c.c.), Ac_2O (50 c.c.), and AcOH (100 c.c.) during 1 hr. (then further 15 min. stirring) at 20° gives a product (81%), hydrolysed (aq. H_2SO_4) to 3- (32%), 4- (32%), and 5-nitro-*o*-toluidine (31%), which are separated by crystallisation from CCl_4 . $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ (25 g.), HNO_3 (d 1.45; 103.3 c.c.), conc. H_2SO_4 (109.9 c.c.), and AcOH (100 c.c.) at 15° similarly afford a product (83.8%) and thence 4- (11%) and 6-nitro-*m*-toluidine (82%). $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ (25 g.; addition 1 hr., further stirring 1 hr.) with HNO_3 (d 1.45; 68.9 c.c.) and Ac_2O (132.8 c.c.) at 35° gives a product (90.4%), hydrolysed to 3-nitro- (92%) and 3:5-dinitro-*p*-toluidine (6.5%). Other nitration conditions are investigated. H. B.

Mono- and di-bromination of heteronuclear-substituted 4-acetamidodiphenyls. F. H. CASE (J. Amer. Chem. Soc., 1939, 61, 767–770).—When 2-bromo- and 2- or 3-nitro-4'-acetamidodiphenyl are mono- and di-brominated, Br enters the $\text{C}_6\text{H}_4\cdot\text{NHAc}$ ring. $2\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot 4'$ (I) with Br (1 mol.) in $\text{NaOAc}\text{--}\text{AcOH}$ gives 2:3'-dibromo-4'-acetamidodiphenyl, m.p. 161–162°, hydrolysed by $\text{HBr}\text{--}\text{EtOH}$ to 2:3'-dibromo-4'-aminodiphenyl (II), m.p. 69–70°. With $\text{Br}\text{--}\text{AcOH}$, (II) gives 2:3':5'-tribromo-4'-aminodiphenyl, m.p. 100–101° [Ac derivative (III), m.p. 223–224°], also obtained from $2\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 4'$ and converted by $\text{NaNO}_2\text{--}\text{H}_2\text{SO}_4\text{--}\text{EtOH}$ into 2:3':5'-tribromodiphenyl, m.p. 68–69° (cf. Bellavita, A., 1938, II, 9), which with CrO_3 gives 3:5:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CO}_2\text{H}$ (IV). With 2 mols. of Br (I) gives (III). 2:4'-Dinitrodiphenyl and $\text{H}_2\text{--PtO}_2\text{--EtOH}$ give NO_2 -amines, converted by hot AcOH into 2-nitro-4'- (V), m.p. 154–155°, and a little 4-nitro-2'-acetamidodiphenyl, m.p. 199–200°. Bromination of (V) gives 3-bromo- (VI), m.p. 169–170°, or 3:5-dibromo-2'-nitro-4'-acetamidodiphenyl, m.p. 220–221°, according to the conditions. Hydrolysis of (VI) gives 3-bromo-2'-nitro-4'-aminodiphenyl, m.p. 83–84°, converted by Br into 3:5-dibromo-2'-nitro-4'-aminodiphenyl or by NaNO_2 etc. into 3-bromo-2'-nitrodiphenyl (obtained also by deamination of 3-bromo-2'-nitrobenzidine). 3:4'-Dinitrodiphenyl and Na_2S_x in dioxan at 80–90° give 3-nitro-4'-aminodiphenyl (VII), m.p. 127–128° (oxidised to $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$), the Ac derivative (VIII), m.p. 189–190° after sintering, of which yields 3-bromo-3'-nitro-4'-acetamidodiphenyl, m.p. 164–165°, hydrolysed to the base (IX), m.p. 110–111°. $\text{Br}\text{--}\text{AcOH}$ converts (VII) or (IX) into 3:5-dibromo-3'-nitro-4'-aminodiphenyl, m.p. 175–176° [Ac derivative, m.p. 255–256°, also obtained in poor yield from (VIII)], which yields 3:5-dibromo-3'-nitro-, m.p. 165–166°, and thence ($\text{SnCl}_2\text{--EtOH}$; acetylation) 3:5-dibromo-3'-acetamido-diphenyl, m.p. 177–178°. Hydrolysis then affords 3:5-dibromo-3'-aminodiphenyl, m.p. 67–68°, oxidised to (IV). $m\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NHAc}$ and HNO_3 (d 1.6) at $<-1^\circ$ give a product, hydrolysed to 4:4'-dinitro-3-aminodiphenyl, m.p. 252–253° (Ac derivative), deaminated to ($p\text{-NO}_2\cdot\text{C}_6\text{H}_4$)₂. 4-Nitro-3'-acetamidodiphenyl is prepared; the derived base is oxidised to $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. R. S. C.

Molecular structure and chemical reaction.
I. Molecular rearrangement of aromatic

amines. S. KATO and F. SOMENO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 35, 399–414).— H_2SO_4 or HCl ppts. the benzidine salt (I) from $(\text{NHPH})_2$ in Et_2O at room temp., 2 mols. of acid being required. 0.002M- HCl in Et_2O and 0.001M- $(\text{NHPH})_2$ at -100° ppt. the dihydrochloride (II) of $(\text{NHPH})_2$, but from 0.01M. solutions at -100° or -9° (I) is formed. At 240° (II) changes to (I). When heated in a capillary tube or kept in Et_2O , $(\text{NHPH})_2$ gives $(\text{NPh})_2$ and H_2 . A 0.001M- Et_2O solution of $\text{NHPH}\cdot\text{N}\cdot\text{NPh}$ with 1 mol. of H_2SO_4 gives $\text{PhN}_2\cdot\text{SO}_3\text{H}$ (and NH_2Ph), which with NH_2Ph in MeOH gives $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ by way of a sulphate, $\text{NPh}\cdot\text{N}\cdot\text{NH}_2\text{Ph}\cdot\text{SO}_3\text{H}$, which differs sterically from that of $\text{NHPH}\cdot\text{N}\cdot\text{NPh}$. $\text{NHPH}\cdot\text{CH}_2\text{Ph}\cdot\text{HCl}$ (III) decomposes at the m.p. (215°) into NH_2Ph and CH_2PhCl ; cooling the melt gives a salt, isomeric with (III), which melts at 198° with rearrangement to $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Ph}$, and is also obtained directly from CH_2PhCl and NH_2Ph at $160\text{--}175^\circ$. Structures are deduced from absorption spectra. The isomerisms depend on which radical or atom is last attached to the N, i.e., which radical is linked by the $2p\sigma$ electrons of the N. Rearrangements of NV derivatives have a common mechanism depending on the acid and differing in case only by virtue of the relative ease of the electronic changes involved; these changes are discussed. R. S. C.

Phenylthiocarbamides. Triad $\text{--N}\cdot\text{C}\cdot\text{S--}$. VIII. Hector's base and its attempted synthesis. K. B. LAL and H. KRALL (J. Indian Chem. Soc., 1939, 16, 31–34; cf. A., 1937, II, 492).—It is suggested that Hector's base (I) (A., 1889, 872) is a direct oxidation product of $\text{NHPH}\cdot\text{CS}\cdot\text{NH}_2$ (II). The yield of (I) from (II), $\text{CN}\cdot\text{NHPH}$ (III) and $\text{EtOH}\text{--}\text{HCl}\text{--}\text{H}_2\text{O}_2$ is $>$ that obtained in absence of (III); (III) appears to be unchanged. $\text{NHPH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ and PhNCS (with or without H_2O_2) give a non-basic compound, m.p. 198° (Ac derivative, m.p. 235°), not oxidised to (I). Diphenylguanidine and KCNS in Et_2O afford the thiocyanate, not oxidised (H_2O_2) to (I). The yield of (I) from (II) and HNO_2 (cf. A., 1936, 198) corresponds with the reaction $2(\text{II}) + 4\text{HNO}_2 \rightarrow \text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ [= (I)] + S + 4NO + $4\text{H}_2\text{O}$. A. T. P.

Action of cupric and cuprous chloride and sodium on thiocarbamilide. N. V. KOSCHKIN (J. Gen. Chem. Russ., 1938, 8, 1083–1090).— $\text{CS}(\text{NHPH})_2$ (I) in EtOH and CuCl or CuCl_2 yield the compounds $\text{CuCl}\cdot\text{CS}(\text{NHPH})_2$ and $\text{CuCl}_2\cdot\text{CS}(\text{NHPH})_2$. (I) and Na yield a Na salt, which with EtCl gives $\text{NHPH}\cdot\text{CS}\cdot\text{NPhEt}$. R. T.

Derivatives of sulphanilamide.—See B., 1939, 551.

Reaction of some aromatic diamines with ethyl malonate. T. N. MEHTA and V. B. THOSAR (J. Indian. Chem. Soc., 1938, 15, 629–632).— $\text{CH}_2(\text{CO}_2\text{Et})_2$ (I) (0.3 mol.) and benzidine (0.1 mol.) at $115\text{--}120^\circ$ give malonylbenzidine, $\text{Et N}\cdot 4\cdot(4'\text{-aminodiphenyl})\text{malonamate}$, m.p. $139\text{--}140^\circ$ [azo- β -naphthol derivative, m.p. 298° (decomp.)], and $\text{Et}_2\text{ NN}\cdot 4\cdot 4'\text{-diphenylenedimalonamate}$, m.p. $>300^\circ$ [hydrolysed ($\text{NaOH}\text{--}\text{EtOH}$) to the acid, m.p. 323--

324° (decomp.), decarboxylated to diacetylbenzidine]. With *o*-toluidine, (I) gives *Et*₂ NN'-3:3'-dimethyl-4:4'-diphenylenedimalonamate, m.p. >300°. With *p*-C₆H₄(NH₂)₂, (I) gives *p*-C₆H₄(NH-CO-CH₂-CO₂Et)₂ [hydrolysed to the acid, m.p. ~300° (decomp. from 250°)] and *Et* *p*-acetamidophenylmalonamate, m.p. >300° [hydrolysed to the acid, m.p. ~300° (decomp.; shrinks at 280°)]; these when heated give *N*-*p*-acetamidophenylmalonimide. E. W. W.

Action of azoxy-compounds on magnesium aryl halides. D. N. KURSANOV, A. S. KURSANOVA, and A. N. BLOCHINA (J. Gen. Chem. Russ., 1938, 8, 1786—1790).—Mg aryl halides react with azoxy-compounds in Et₂O as follows: 2MgRX + NR'NR''O → NR'NR'' + R₂ + (MgX)₂O (R' = Ph, *p*-C₆H₄Me; R = Ph, CH₂Ph, CHPh₂, α -C₁₀H₇). R. T.

Tautomerism of *p*-hydroxyazo-compounds. H. SHINGU (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 35, 78—120).—"Benzeneazoanthranol" (I) with Br in AcOH yields anthraquinone and *p*-C₆H₄Br·N₂Br. Comparison of the absorption spectrum of (I) with those of its *N*-Me and *O*-Ac, m.p. 145°, and -Bz derivatives shows that the stable form is anthraquinonephenylhydrazone, whilst *p*-hydroxyazobenzene has the azo-structure; neither of these is altered by substituents in the Ph group. In benzene-azo- α -naphthol the two forms have much the same stability, the proportion being altered by substituents in the Ph group, or by the nature of the solvent: in EtOH, *p*-NO₂, *o*-CO₂H, *p*-CO₂H, *o*-NO₂, *m*-NO₂, *m*-Cl, *m*-CO₂H, *o*-OMe, *m*-OMe, *p*-Cl, *p*-Br, *o*-OEt, and *m*-Me (in decreasing order of magnitude) favour the hydrazone form, and *p*-OMe, *o*-Me, 2:4:6-Br₃, *p*-Me, and *o*-Cl the azo-form, in general accordance with the electronic theory. The effect of substituents on the λ of the absorption max. has been measured in all three cases, and is discussed. The following compounds are prepared (diazonium salt method): anthraquinone-*p*-methyl-, m.p. 170—171°, -*p*-methoxy-, m.p. 183—184°, -*m*-nitro-, m.p. 210—211.5°, and -*o*-nitro-phenylhydrazone, m.p. 227—228°; *p*-, m.p. 230—230.5° (decomp.), *m*-, m.p. 220—221.5° (decomp.), and *o*-chloro-, m.p. 184—185.5°, *m*-methyl-, m.p. 198—199° (decomp.), and *p*-, m.p. 167—168° (decomp.), *o*-, m.p. 164—165°, and *m*-methoxybenzeneazo- α -naphthol, m.p. 187.5—188.5°. Data for other substituted benzeneazo- α -naphthols are given. A. LI.

***N*-Halogenoamines. II. Sodium and potassium salts of azobenzene-*p*-sulphonbromoamide.** A. CHRZASZCZEWSKA and R. SZTABZYB (Rocz. Chem., 1938, 18, 439—442).—The salts (NPh·N·C₆H₄·SO₂·NMBR)₂·3H₂O (M = Na, K) are obtained from the sulphonamide and MOBr. R. T.

Hydroxy- and amino-azo-nitro-compounds. I. Adsorption of *p*-nitrobenzeneazo- α -naphthol on magnesium hydroxide. L. KULBERG (J. Gen. Chem. Russ., 1938, 8, 1132—1138).—1:4-OH·C₁₀H₆·N₂·C₆H₄·NH₂·*p* (I) boiled with Na₂CO₃ yields a blue Na salt [as (II)], which dissolves in H₂O to a yellow solution (quinone-*p*-nitrophenylhydrazone

form), changing to violet on boiling, and extraction of this solution with xylene gives a red (*p*-nitrobenzeneazonaphthol) form. The colour change of the violet solution of (II) due to adsorption on Mg(OH)₂ is ascribed to selective adsorption of (II). R. T.

Anaphylaxis with chemically known substances. H. E. FIERZ-DAVID, W. JADASSOHN, and A. KLEEMANN (Helv. Chim. Acta, 1939, 22, 3—18; cf. A., 1937, II, 528).—Under apparently identical conditions, guinea-pigs pretreated with succinilic acid-azoprotein (I) are occasionally protected against anaphylactic shock with bis-*p*-succinilic acid-azoresorcinol-F (II), whilst in other cases this effect is not produced but the sp. supersensitiveness is neutralised by (II) in guinea-pigs pretreated and certainly sensitised with (I). Oleyl-*N*-methyltaurine causes in normal animals, though less frequently than in those which have been pretreated, a neutralisable contraction of the surviving uterus. The differences noted previously (cf. A., 1937, II, 144) between bis-*p*-succinilic acid-azoresorcinol-L (III) (Landsteiner) and (II), which are prepared by different methods, are due to position isomerism; fission with Sn and conc. HCl shows that (II) and (III) are 2:4- and 4:6-bisazoresorcinol dyes, respectively. The Ac derivative, m.p. 180°, of 4:6:1:3-(NH₂)₂C₆H₂(OH)₂ is the Ac₆ compound. Tetra-acetyl-*p*-phenylenediamine has m.p. 207°. Acetylation (Ac₂O) of 1:3:2:4-(OH)₂C₆H₂(NH₂)₂·2HCl and dry distillation of the product gives 1:1'-dimethylbenzodioxazole, m.p. 111° (lit. 192°). H. W.

Action of hydrazine, methylhydrazine, and dimethylhydrazine on halogenonitrobenzenes. B. VIS (Rec. trav. chim., 1939, 58, 387—410).—NHMe·NH₂ and 1:2:4-C₆H₃Cl(NO₂)₂ (I) give α -2:4-dinitrophenyl- α -methylhydrazine (cf. A., 1936, 1103), oxidised (aq. KMnO₄, EtOH) to 2:4:1-(NO₂)₂C₆H₃·NHMe. The 2:4-dinitrophenylmethylhydrazones of the following are described: CH₂O, m.p. 87°, EtCHO, m.p. 105°, PrⁱCHO, m.p. 78°, Pr^sCHO, m.p. 105°, *p*-C₆H₄Pr^sCHO, m.p. 201°, CHPh·CH·CHO, m.p. 184°, CH₂Ph·CHO, m.p. 139°, CPhMe, m.p. 156°. (I) and NMe₂·NH₂ or (·NHMe)₂ in EtOH give α -2:4-dinitrophenyl- β - β -dimethylhydrazine, m.p. 109°, or α -2:4-dinitrophenyl- α - β -dimethylhydrazine, m.p. 105°, respectively, neither reacting with PhCHO (absence of free NH₂). NHMe·NH₂ and 1:4:2-C₆H₃Cl₂·NO₂ (II) or 1:4:2-C₆H₃Br₂·NO₂ (III) give α -4-chloro-2-nitrophenyl- or α -4-bromo-2-nitrophenyl- α -methylhydrazine, respectively (cf. A., 1937, II, 187). The 4-chloro-2-nitro- and 4-bromo-2-nitro-phenylmethylhydrazones, respectively, of the following are described: CH₂O, m.p. 205°, 203°, COMe₂, m.p. 147°, 158°, Ac₂O, m.p. 165°, 169° (? Ac derivatives), COEt₂, m.p. 142°, 146°, COMe·C₆H₁₃, m.p. 140°, 97°, CH₂Ac·CO₂Et, m.p. 154°, 162°, CPhMe, m.p. 125°, 123°, CH₂Ph·CHO, m.p. 138°, 141°, *p*-OH·C₆H₄·CHO, m.p. 164°, 189°, *p*-C₆H₄Me·CHO, m.p. —, 125°, *p*-C₆H₄Pr^s·CHO, m.p. 133°, 129°. There was no reaction between (II) or (III) and NMe₂·NH₂ or

(NHMe)₂ at 100°. N₂H₄ or NHMe·NH₂ and 1:3:4:6-C₆H₂Cl₂(NO₂)₂ (IV) give 4:6:1:3-(NO₂)₂C₆H₂(NH·NH₂)₂ [oxidised (KMnO₄) to m-C₆H₄(NO₂)₂] or 4:6:1:3-(NO₂)₂C₆H₂(NMe·NH₂)₂, respectively (cf. A., 1937, II, 494). The 4:6-dinitrophenyl-1:3-dihydrazones and 4:6-dinitrophenyl-1:3-di-(α -methyl)hydrazones, respectively, of the following are described: MeCHO, m.p. 308—310°, 206°, COMe₂, m.p. —, 98°, COEt₂, m.p. 225°, 85°, COMe·C₆H₁₃, m.p. 170°, 96°, *n*-C₆H₁₃·CHO, m.p. 208° and 224°, —, CH₂Ac·CO₂Et, m.p. —, 90°, CH₂Ph·CHO, m.p. 204°, 151°, PhCHO, m.p. —, 236°, *o*-, m.p. 302° and 312°, 249°, *m*-, m.p. 342°, 241°, and *p*-C₆H₄Cl·CHO, m.p. 377°, 244°, *o*-, m.p. 331°, 288°, *m*-, m.p. 376°, 340°, and *p*-NO₂·C₆H₄·CHO, m.p. 398°, 318°, *p*-OH·C₆H₄·CHO, m.p. —, 254°, *p*-OMe·C₆H₄·CHO, m.p. —, 202°, *p*-C₆H₄Me·CHO, m.p. 309°, 211°, *p*-C₆H₄Pr^{*β*}·CHO, m.p. 354°, 230°, vanillin, m.p. 343°, 287°, piperonal, m.p. 345°, 272°, 5-methyl-, m.p. 252°, 231°, and 5-hydroxymethyl-furfuraldehyde, m.p. 242—245°, 158°. (IV) and NMe₂·NH₂ give α -3-chloro-4:6-dinitrophenyl- $\beta\beta$ -dimethylhydrazine (V), m.p. 121°, whence α -3-methoxy-, m.p. 151°, -3-ethoxy-, m.p. 177°, -3-methylamino-, m.p. 179°, -3-anilino-, m.p. 189°, and 3-phenylhydrazino-4:6-dinitro- $\beta\beta$ -dimethylhydrazine, m.p. 218°, are obtained. (IV) and (NHMe)₂ give α -3-chloro-4:6-dinitrophenyl- $\alpha\beta$ -dimethylhydrazine (VI), m.p. 141°, whence the corresponding 3-ethoxy-, m.p. 119°, and 3-methylamino-derivative, m.p. 180°. (V) and N₂H₄ or NHMe·NH₂ give 4:6-dinitro-3- $\beta\beta$ -dimethylhydrazinophenylhydrazine, m.p. 206° [oxidised by aq. EtOH-FeCl₃ to 4:6:4':6'-tetranitro-3:3'-di-($\beta\beta$ -dimethylhydrazino)azoxybenzene, m.p. 194°, and by KMnO₄ to 4:2:1-(NO₂)₂C₆H₃·NH·NMe₂], or α -4:6-dinitro-3- $\beta\beta$ -dimethylhydrazinophenyl- α -methylhydrazine, m.p. 169°, respectively. The 4:6-dinitro-3-($\beta\beta$ -dimethylhydrazino)phenylhydrazones and 4:6-dinitro-3-($\beta\beta$ -dimethylhydrazino)phenyl- α -methylhydrazones, respectively, of the following are described: CH₂O, m.p. 247°, 143°, MeCHO, m.p. 262°, 130°, COMe₂, m.p. 217°, 145°, Ac₂O, m.p. 261°, 213° (? Ac derivatives), COEt₂, m.p. 145°, 138—141°, COMe·C₆H₁₃, m.p. 128°, 72°, *n*-C₆H₁₃·CHO, m.p. 156°, 63° and 82°, CH₂Ac·CO₂Et, m.p. 163°, 103°, COPhMe, m.p. 251°, 151°, CH₂Ph·CHO, m.p. 175°, 143°, PhCHO, m.p. 259°, 182°, *o*-, m.p. 264°, 211°, *m*-, m.p. 261°, 170°, and *p*-C₆H₄Cl·CHO, m.p. 275°, 220°, *o*-, m.p. 258°, 225°, *m*-, m.p. 262°, 242°, and *p*-NO₂·C₆H₄·CHO, m.p. 301°, 247°, *o*-, m.p. 284°, 204°, and *p*-OH·C₆H₄·CHO, m.p. 289°, 220°, *p*-OMe·C₆H₄·CHO, m.p. 242°, 220°, *p*-C₆H₄Me·CHO, m.p. 250°, 169°, *p*-C₆H₄Pr^{*β*}·CHO, m.p. 232°, 155°, vanillin, m.p. 235°, 179°, piperonal, m.p. 248° and 264°, 244°, furfuraldehyde, m.p. 255° and 298°, 232°, 5-methyl-, m.p. 263°, 184°, and 5-hydroxymethyl-furfuraldehyde, m.p. 243°, 109—116°. (VI) and N₂H₄ or NHMe·NH₂ give 4:6-dinitro-3- $\alpha\beta$ -dimethylhydrazinophenylhydrazine, m.p. 181°, or 4:6-dinitro-3- $\alpha\beta$ -dimethylhydrazinophenyl- α -methylhydrazine, m.p. 165°, respectively. The corresponding hydrazones, respectively, of the following are described: PhCHO, m.p. 238°, 158°, furfuraldehyde, m.p. 209°, 178°. NMe₂·NH₂ and 1:3-dichloro- (VII) or 1:3-dibromo-4:5-dinitrobenzene (VIII) give $\alpha\alpha$ -di-(4:6-dichloro-

2-nitrophenyl)- $\beta\beta$ -dimethylhydrazine, m.p. 165°, or $\alpha\alpha$ -di-(4:6-dibromo-2-nitrophenyl)- $\beta\beta$ -dimethylhydrazine, m.p. 173°, respectively. (NHMe)₂ and (VII) or (VIII) give $\alpha\beta$ -di-(4:6-dichloro-2-nitrophenyl)- $\alpha\beta$ -dimethylhydrazine, m.p. 156°, or $\alpha\beta$ -di-(4:6-dibromo-2-nitrophenyl)- $\alpha\beta$ -dimethylhydrazine, m.p. 152°, respectively. S. H. H.

Preparation of *m*-bromophenol. C. F. KOELSCH (J. Amer. Chem. Soc., 1939, 61, 969).—*m*-C₆H₄Br·OH is obtained in 77·8% yield from *m*-C₆H₄·N₂·HSO₄ by hot, aq. H₂SO₄. R. S. C.

Structure of amyphenols. Z. N. NAZAROVA (J. Gen. Chem. Russ., 1938, 8, 1336—1340).—COPhBu^{*β*} is reduced to CH₂Ph·CH₂Pr^{*β*} (I), which is sulphonated (oleum at room temp.), and the sulphonation product is fused with KOH, to yield *p*-isoamyphenol (II), b.p. 245—250° (*Me ether*, b.p. 225—230°; *acetate*, b.p. 250—255°; *benzoate*, b.p. 345—347°); (II) is also obtained via the NO₂, NH₂, and diazo-derivatives of (I), or by reduction of *p*-hydroxyvalerophenone. The SO₃H-derivative of CHPhMe·CHMe₂ fused with KOH yields *p*- α -methyl-isobutylphenol (III), b.p. 245—250° (*Me ether*, b.p. 228—232°). Commercial *iso*-C₅H₁₁·OH (IV) and PhOH (AlCl₃) heated at 160° for 3 hr. yield (III) and *p*-*tert*-amyphenol; it follows that (IV) is a mixture of β - and γ -methylbutanol. R. T.

Nitration by means of nitrogen peroxide. IV. Phenols and aromatic amines. P. P. SCHORIGIN and A. V. TOPRSCHIEV (J. Gen. Chem. Russ., 1938, 8, 986—990).—PhOH and N₂O₄ at 0—154° give 2:4-(NO₂)₂C₆H₃·OH (I), *m*-cresol and N₂O₄ (0—100°) afford 4:6-dinitro- and 2:4:6-trinitro-*m*-cresol, β -C₁₀H₇·OH (0—60°) gives 1:6:2-(NO₂)₂C₁₀H₅·OH, NH₂Ph (0° and at room temp.) gives (I) and *p*-NO₂·C₆H₄·NH₂, NPhMe₂ (0—60°) gives *p*-NMe₂·C₆H₄·NO₂, and NPhAc (60—70°) affords *o*- and *p*-NO₂·C₆H₄·NHAc. R. T.

Demonstration of participation of free radicals in rearrangement of phenyl benzyl ether. W. J. HICKINBOTTOM (Nature, 1939, 143, 520).—Hydroxyphenylquinolines are also formed when CH₂Ph·OPh (I) is heated in quinoline at ~250° (cf. A., 1939, II, 59), and by controlling conditions of reaction the yields of benzyl- and hydroxyphenyl-quinolines can be increased considerably at the expense of the normal products of the rearrangement. This evidence supports the view that the preliminary phase of the reaction is a dissociation of (I) into CH₂Ph and OPh radicals. L. S. T.

Application of cyclo-dehydration reactions to some safrole derivatives. R. M. ORCUTT and M. T. BOGERT (Rocz. Chem., 1938, 18, 732—738).—Safrole is oxidised (KMnO₄) to safrole glycol (I) and homopiperonylic acid. (I) is oxidised with Pb(OAc)₄ to homopiperonal, which with CH(OEt)₃ in EtOH-HCl gives β -3:4-methylenedioxyphenylacetaldehyde Et₂ acetal, m.p. 50—51°, and with Mg cyclohexyl chloride gives cyclohexylpiperonylcarbinol, m.p. 82·5—83·5°. This with KHSO₄ at 175—225° yields homopiperonylidene-cyclohexane (II), b.p. 150°/2 mm., converted by shaking with 85% H₂SO₄ into 6:7-methylenedioxy-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p.

182—186°/12 mm. Homopiperonyl alcohol (*phenylurethane*, m.p. 98—99°) and PBr_3 at 0° yield *homopiperonyl bromide*, b.p. 150°/10 mm., which with COMe_2 and Mg in Et_2O gives *homopiperonyldimethylcarbinol* (III), b.p. 170°/18 mm. (*phenylurethane*, m.p. 116—117°), together with $\alpha\beta$ -dipiperonylethane, m.p. 69°, whilst with cyclohexanone and Mg the product is *homopiperonylcyclohexan-1-ol*, m.p. 87—88°, dehydrated (KHSO_4) to (II). (III) and 85% H_2SO_4 at -7° give 5 : 6-methylenedioxy-1 : 1-dimethylindane, b.p. 132°/15 mm., oxidised by aq. KMnO_4 to 4 : 5-methylenedioxy- $\alpha\alpha$ -dimethylhomophthalic acid, m.p. 147—150°.

R. T.

Specificity of synthetic oestrogenic compounds.

E. KERSCHBAUM, A. KLEEDORFER, F. PRILLINGER, F. WESSELY, and E. ZAJIC (*Naturwiss.*, 1939, 27, 131—132; cf. Dodds *et al.*, A., 1938, III, 299; Campbell *et al.*, A., 1939, III, 264).—Single injections of the following compounds in *Et oleate* produce full oestrus in 100% of adult castrated rats in the doses given: γ -hydroxy- $\gamma\delta$ -di-*p*-hydroxyphenyl-*n*-hexane (I), m.p. 232° (obtained by demethylation of its Me_2 ether), 50 μg ., and its 4 : 4'-diacetate, m.p. 155°, 25 μg .; 4 : 4'-diacetoxy- $\alpha\beta$ -diethylstilbene oxide (II), m.p. 104°, 1 μg .; $\gamma\delta$ -di-*p*-hydroxyphenyl-*n*-hexane (III), m.p. 185°, 2 μg ., and its diacetate, m.p. 139°, 1 μg .; 4 : 4'-dihydroxy- $\alpha\beta$ -diethylstilbene (IV), 1 μg ., and its diacetate, 1 μg .; oestrone, 3 μg . 4 : 4'-Dihydroxy- $\alpha\beta$ -diethylstilbene oxide (V), decomp. 145°, in doses of 4 μg . produces full oestrus in 50% of the rats. Oestrus is not produced by 16 μg . of $\alpha\alpha$ -di-*p*-hydroxyphenyl-propyl *Et ketone* (VI) or by 32 μg . of its diacetate, m.p. 91°. (II), (V), and 4 : 4'-dimethoxy- $\alpha\beta$ -diethylstilbene oxide (VII), m.p. 119°, are obtained by the action of BzO_2H on the corresponding stilbenes. Hydrogenation of (VII) gives 30% of $\gamma\delta$ -di-*p*-anisyl-*n*-hexane (VIII), m.p. 146°, together with the Me_2 ether, m.p. 117°, of (I) and, by rearrangement without reduction, the Me_2 ether of (VI). (VIII) is also obtained in ~100% yield by reduction (Pd-H_2) of liquid 4 : 4'-dimethoxy- $\alpha\beta$ -diethylstilbene (IX). (IX) treated with I yields a solid isomeride, m.p. 124°. (IX) is probably a *cis*- and its isomeride, (IV), and the above oxides are probably *trans*-compounds. (VIII), (III) and its diacetate are probably *meso*-compounds.

W. MCC.

Additive products of diphenols. Y. GARREAU (*Compt. rend.*, 1939, 208, 1158—1160; cf. A., 1938, II, 96, 136).— $p\text{-C}_6\text{H}_4(\text{OH})_2$ (0.9 mol.) is added to a solution of $(\text{CH}_2\text{-NH}_2)_2$ (= en; 3.2 mols.) and metallic halide (1.2 mols.) in N_2 , thus giving compounds, $3\text{C}_6\text{H}_4(\text{OH})_2\cdot 2\text{en}\cdot \text{M}\cdot 2\text{H}_2\text{O}$ (M = Cu, Zn, or Cd). Similarly constituted compounds containing varying amounts of H_2O of crystallisation are formed when M = Ni, Co, or Ca. The compounds $3p\text{-C}_6\text{H}_4(\text{OH})_2\cdot 5\text{en}\cdot \text{Zn}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ and $m\text{-C}_6\text{H}_4(\text{OH})_2\cdot 3\text{en}\cdot \text{ZnI}_2$ are obtained using ZnI_2 . The compounds, $\text{Co}_2(\text{C}_6\text{H}_5\text{O}_2)_2\cdot \text{en}$, and $\text{Cu}(\text{C}_6\text{H}_4\text{O}_2)_2\cdot \text{en}\cdot 2\text{H}_2\text{O}$, are obtained from $o\text{-C}_6\text{H}_4(\text{OH})_2$ and $\text{CoCl}_2(\text{CoBr}_2)$ and CuCl_2 , respectively.

J. L. D.

Spectrographic study of the action of alkalis on resorcinol. I. Resorcinol and its methyl ether. II. Dihydroresorcinol and resorcinol in sulphurous acid solution. III. Diphenyl deriv-

atives. N. A. VALJASCHKO and M. M. SCHTSCHERBAK (*J. Gen. Chem. Russ.*, 1938, 8, 1597—1628, 1629—1640, 1641—1662).—I. Absorption spectra ($\lambda\lambda$ 1900—5000) are given for $m\text{-C}_6\text{H}_4(\text{OH})_2$ (I) and $m\text{-OH-C}_6\text{H}_4\text{-OMe}$ in H_2O and EtOH , and in presence of NaOH and NaOEt . The changes caused by addition of aq. NH_3 are initially the same as with NaOH , but with time profound changes in the structure of (I) take place.

II. The absorption spectrum of Δ^1 -cyclohexen-1-ol-3-one in EtOH is analogous to that of (I) in aq. SO_2 , whence it is concluded that the compounds are structurally similar. Differences in EtOH - NaOEt are observed.

III. Absorption spectra are given for ($p\text{-OH-C}_6\text{H}_4$) $_2$, diphenoquinone (II), and diphenoquinhydrone (III) in EtOH and EtOH - NaOEt . In alkaline solution (II) undergoes partial reduction to (III), (I) undergoes oxidation to 2 : 2'-dihydroxydiphenoquinone, and (I) and (II) combine to give diphenoquinoresorcinol.

R. T.

Extractives of pine heart wood. H. ERDTMAN (*Naturwiss.*, 1939, 27, 130—131).—The "acetone resin" obtained from the wood, when purified by adsorption on Al_2O_3 and fractionally cryst. yields 3 : 5-dihydroxystilbene (I) (pinosylvin), m.p. 155.5—156° [dibenzoate, m.p. 150—151°; diacetate, m.p. 100—101°; Me_2 ether (II), m.p. 56—57°], and its Me ether (III), m.p. 122° (benzoate, m.p. 84.5—86°). (II) on hydrogenation takes up 2 H yielding an oil [Br_2 -derivative (IV), $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Br}_2$, m.p. 141—142°], and on bromination gives the Br_2 -derivative dibromide, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Br}_4$, converted into (IV) by $\text{Zn} + \text{AcOH}$. KMnO_4 oxidises (II) to BzOH and 3 : 5 : 1-($\text{OMe})_2\text{C}_6\text{H}_3\text{-CO}_2\text{H}$. The (I) + (III) content of the dry wood is 0.5—1%. At a concn. of 0.002% (I) is toxic to fish. The wood if extracted with COMe_2 is normally degraded by sulphite, but is not so degraded if afterwards impregnated with (I). W. MCC.

Nuclear methylation of phenols. Synthesis of intermediates in the preparation of anti-sterility factors. W. T. CALDWELL and T. R. THOMPSON (*J. Amer. Chem. Soc.*, 1939, 61, 765—767).—*s*-*m*-Xylenol, NHMe_2 (1 mol.), and CH_2O (1 mol.) in H_2O at 25—35° give 4-dimethylaminomethyl-*s*-*m*-xylenol, m.p. 42—42.5°, converted by hydrogenolysis (Cu chromite) in dioxan at 165°/177 atm. into 2 : 3 : 5 : 1- $\text{C}_6\text{H}_2\text{Me}_3\text{-OH}$, m.p. 93°. Coupling with $p\text{-SO}_3\text{H-C}_6\text{H}_4\text{-N}_2\text{Cl}$ in NaOH and reduction by $\text{Na}_2\text{S}_2\text{O}_4$ then gives 4 : 2 : 3 : 5 : 1- $\text{NH}_2\text{-C}_6\text{HMe}_3\text{-OH}$, oxidised by FeCl_3 to ψ -cumoquinone, which with $\text{Na}_2\text{S}_2\text{O}_4$ gives 2 : 3 : 5-trimethylquinol (27% over-all yield), m.p. 169—170°. With 3 mols. each of NHMe_2 and CH_2O , quinol gives only 2 : 5-bis(dimethylaminomethyl)quinol, m.p. 190°, recognised by hydrogenolysis to 2 : 5 : 1 : 4- $\text{C}_6\text{H}_2\text{Me}_2(\text{OH})_2$, m.p. 208°, which with FeCl_3 gives the quinone, m.p. 123—124°. R. S. C.

3-Nitro- and 3-amino-4-hydroxybenzenesulphonamide. W. O. KERMACK, W. T. SPRAGG, and W. TEBRICH (*J.C.S.*, 1939, 608—610).—*p*-Hydroxybenzenesulphonamide (from the NH_2 -compound) (*Na* salt + $2\text{H}_2\text{O}$, m.p. 276°) with HNO_3 (*d* 1.42) and conc. H_2SO_4 at $<0^\circ$ and then at room temp. yields 3-nitro-4-hydroxy- (I), m.p. 210° (*Na* salt, explodes 330°), re-

duced ($\text{Na}_2\text{S}_2\text{O}_4$) to 3-amino-4-hydroxy-benzenesulphonamide, m.p. 202° . Nitration of $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ yields 3-nitro-4-acetamidobenzenesulphonyl chloride, m.p. 104° . This with aq. NH_3 gives the amide, m.p. 186° , hydrolysed (dil. HCl) to 3:4:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{SO}_2\cdot\text{NH}_2$, which when boiled with aq. 10% NaOH yields (I). A. Li.

Sulphonation with sulphites. III. Simultaneous oxidation of sodium sulphite and β -naphthol and its derivatives. S. V. BOGDANOV and V. A. IVANOVA (J. Gen. Chem. Russ., 1938, 8, 1071—1082).—2:3- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ and aq. Na_2SO_3 heated with MnO_2 at 130° yield 2-hydroxy-1-sulpho-3-naphthoic acid, and 2:6- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ similarly yields 2:1:6- $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$; the general reaction is: $\text{RH} + \text{Na}_2\text{SO}_3 + \text{O} \rightarrow \text{R}\cdot\text{SO}_3\text{Na} + \text{NaOH}$. At the same time part of the Na_2SO_3 undergoes oxidation to Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_6$, but these reactions are independent of that of sulphonation. The sulphonation reaction ceases with time, owing to increasing $[\text{NaOH}]$ of the medium. β -Naphtholsulphonic acids accelerate oxidation of Na_2SO_3 by MnO_2 , but retard oxidation by O_2 . R. T.

Aromatic sulphone-sulphonic acids. H. KUCZYŃSKI, L. KUCZYŃSKI, and E. SUCHARDA (Rocz. Chem., 1938, 18, 625—650).— $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{SO}_2\text{Cl}$, Ph_2 , and AlCl_3 in CCl_4 give di- p -diphenyl sulphone, m.p. 216° (lit. 206°), which is also obtained, together with 4:4'-bis- p -diphenylsulphonyldiphenyl, m.p. 345° (decomp.), from Ph_2 and H_2SO_4 (6 hr. at the b.p.). 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, Ph_2 , and P_2O_5 (10 hr. at 160°) yield p -diphenyl β -naphthyl sulphone, m.p. 138° . C_{10}H_8 heated with H_2SO_4 yields di- β -naphthyl sulphone (I), m.p. 177° . $m\text{-C}_6\text{H}_4(\text{SO}_2\text{Ph})_2$, 1-benzenesulphonyl-3-naphthalenesulphonylbenzene, m.p. 155° , 2:7-bis-(m -4-xylenesulphonyl)naphthalene, m.p. 212° , 4:4'-bisnaphthalenesulphonyldiphenyl, m.p. 229° , and 2:6-bis- $\alpha\beta$ -naphthalenesulphonylnaphthalene, m.p. 316° , were prepared analogously. The monosulphonic acids of the above sulphones, and of m -xylyl β -naphthyl sulphone, m.p. 118° (lit. 128°), have been prepared by heating with ClSO_3H in CCl_4 solution; (I) similarly gives a mixture of products, of which the following were identified: 2:2'-dinaphthyl sulphone-8- (chloride, m.p. 168° ; anilide, m.p. 188°), and -5-mono- (chloride, m.p. 166° ; anilide, m.p. 184°), and -8:8'-di-sulphonic acid (Ba , $+5\text{H}_2\text{O}$, Na , $+6\text{H}_2\text{O}$, Pb salt, $+6.5\text{H}_2\text{O}$; dichloride, m.p. 247°). 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ undergoes condensation when heated alone or with P_2O_5 , H_3PO_4 , or H_2SO_4 (24 hr. at 160°), to yield a mixture of 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}\cdot 2$ and 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}\cdot 2$. R. T.

Epimeric alcohols of the cyclohexane series. I. *cis*- and *trans*-Dihydrocryptol. R. G. COOKE, D. T. C. GILESPIE, and A. K. MACBETH (J.C.S., 1939, 518—522; cf. A., 1939, II, 17).—Separation of *cis*-(I), b.p. $72^\circ/1.9$ mm. [hydrate (3.5 H_2O), transition temp. $34.2\text{—}34.4^\circ$; H phthalate, m.p. 130° ; acetate, b.p. $70.5^\circ/1.1$ mm.], and *trans*-dihydrocryptol (II), b.p. $79.5^\circ/1.8$ mm. (H phthalate, m.p. 115° ; acetate, b.p. $76^\circ/2$ mm.), is effected through their Mg phthalates (the *trans*-salt, m.p. $127\text{—}128^\circ$, being the less sol. in H_2O); *d* and *n* (of the alcohols) and rates of hydrolysis of the H phthalates and acetates indicate the

above configurations. Reduction of cryptone (III) with H_2 -Raney Ni-EtOH at $120^\circ/100$ atm. gives essentially (I); Cu-Ba-Cr oxide similarly affords a 60:40 mixture of (I) and (II). Dihydrocryptone [or (III)] with $\text{PtO}_2/70$ atm. yields (II) (90%) and (I) (10%); Ponndorf or Na-EtOH reduction gives essentially (II). A. Li.

$\alpha\beta$ -Diarylacetylene glycols [$\alpha\beta$ -dihydroxy- $\alpha\beta$ -diarylethylenes]. New type of enediol. R. C. FUSON and J. CORSE (J. Amer. Chem. Soc., 1939, 61, 975).—(2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}$) $_2$ (I) or 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COCl}$ with Mg + MgI_2 gives $\alpha\beta$ -dihydroxy- $\alpha\beta$ -dimesitylethylene, m.p. $144\text{—}145^\circ$ (sealed tube in N_2), which is stable in N_2 , oxidises in O_2 to (I), is converted by HCl or piperidine into $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_2\text{Me}_3$, reduces Tollens' reagent or $\text{Cu}(\text{OAc})_2$ at 0° or Na 2:6-dichlorobenzenone-indophenol. [2:4:6- $\text{C}_6\text{H}_2\text{Et}_3\cdot\text{C}(\text{OH})_2$] is prepared from the chloride and is even more stable. R. S. C.

Structure and absorption spectra of hydroxy-triphenylmethane dyes. Isomeric forms of hydroxyfuchsones. P. RAMART-LUCAS (Compt. rend., 1939, 208, 1094—1096).—Fuchsones (I), sulphonephthalein (both in EtOH), and tetrabromophenolphthalein (as ester in C_6H_6) have similar absorption spectra and hence similar structures. The spectra of CHPh_3 and $\text{CPh}_3\cdot\text{OH}$ are nearly identical. The phenolic OH in $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$ (II) produces a normal bathochromic effect, but dehydration of (II) leads to (I) with a large change in absorption. The spectra of benzaurin (III) and aurin (IV) and their OMe-derivatives are displaced towards the visible region compared with that of (I); they have quinonoid structures. In CHCl_3 , (III) exists in the quinonoid form and in another form having a different spectrum. In EtOH, (IV) exhibits the spectrum of the quinonoid form, but in alkali it is much changed. J. L. D.

[Preparation of iodo-compounds of sterols from sterol alcohols.] B. HELFERICH and E. GÜNTHER (Ber., 1939, 72, [B], 932; cf. A., 1939, II, 157).—Cholesteryl iodide has been described previously by Heilbron *et al.* (A., 1936, 1105). H. W.

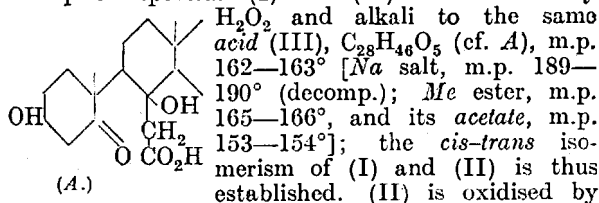
Chemical activation of sterols. V. Relationship between chemical activation and configuration of various sterols and derivatives. VI. Reagents in chemical activation and in sterol colour reactions. J. C. ECK and B. H. THOMAS (J. Biol. Chem., 1939, 128, 257—265, 267—278; cf. A., 1937, III, 364).—V. Of the 24 compounds tested, only ψ -cholestene, $\Delta^{4:6}$ -cholestadiene, 7-dehydrocholestene isomeride, *allo*-, ψ -, and *i*-cholesterol, and compound $\text{C}_{19}\text{H}_{30}\text{O}$ (de Fazi *et al.*, A., 1937, II, 147) yield active products with $\text{H}_2\text{SO}_4\text{--Ac}_2\text{O}$. Ergosterol, stigmasterol, and β -sitosterol give products possessing slight antirachitic activity. The above and previous results (A., 1937, III, 156) show that such treatment activates compounds containing a Δ^4 - or Δ^5 -double linking (with or without an additional one or a OH) without CO at 3 or 7.

VI. Cholestene, cholesterol, and cholesterylene (I) give antirachitic products (increasing activity in the order quoted) with H_2SO_4 , $\text{H}_2\text{SO}_4\text{--Ac}_2\text{O}$, ZnCl_2 (\pm other reagents), and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ in the hot, but not

with SbCl_3 , SbCl_5 , AsCl_3 , or HNO_3 ; max. activity is obtained with anhyd. reagents, and irradiation of the mixture accelerates the change. $\text{H}_2\text{SO}_4\text{-Ac}_2\text{O}$ and AcCl-ZnCl_2 are the most effective reagents for (I). Chemical activation is usually but not always correlated with the production of colour. Sterol colour reactions are reviewed.

A. LI.

Degradations of ergosterol. HUANG-MINLON (Ber., 1939, 72, [B], 854—859).—Ergostadienetriol is oxidised by $\text{Pb}(\text{OAc})_4$ to a less freely sol. aldehyde (I), m.p. 163—164°, $[\alpha]_D^{20} +128^\circ$ in CHCl_3 , which does not give a cryst. oxime, in addition to Heilbron's aldehyde (II), new m.p. 159—160°, $[\alpha]_D^{20} +144^\circ$ in CHCl_3 [oxime, m.p. 195—196° (decomp.)] (cf. Heilbron *et al.*, A., 1933, 500). (I) and (II) have almost identical absorption spectra. (I) and (II) are oxidised by



H_2O_2 and alkali to the same acid (III), $\text{C}_{28}\text{H}_{46}\text{O}_5$ (cf. A), m.p. 162—163° [Na salt, m.p. 189—190° (decomp.)]; Me ester, m.p. 165—166°, and its acetate, m.p. 153—154°; the *cis-trans* isomerism of (I) and (II) is thus established. (II) is oxidised by $\text{KOH-H}_2\text{O}_2$ in MeOH to a neutral substance, m.p. 188—189°, which is oxidised further to (III). KOH-MeOH alone and (I) afford a neutral compound, decomp. 90—92° after softening $\sim 50^\circ$, the oxime, m.p. 219—220° (decomp.), of which appears to indicate the existence of a further isomeric aldehyde. With KI in AcOH (III) appears to yield a lactone, $\text{C}_{28}\text{H}_{46}\text{O}_4$, m.p. 95—98° after softening, converted by alkali followed by acid into a substance, $\text{C}_{28}\text{H}_{46}\text{O}_4$, m.p. 227—228°, which does not dissolve in aq. Na_2CO_3 .

H. W.

Hydrocarbon, $\text{C}_{30}\text{H}_{62}$, and isomeric medicagosterols, $\text{C}_{28}\text{H}_{48}\text{O}, 0.5\text{H}_2\text{O}$, I, m.p. 133°, $[\alpha]_D^{25} -22.5^\circ$ in CHCl_3 (acetate, m.p. 120—121°; 3:5-dinitrobenzoate, m.p. 205°), and II, m.p. 164°, $[\alpha]_D^{25} -2.4^\circ$ in CHCl_3 (acetate, m.p. 173°; 3:5-dinitrobenzoate, m.p. 195°), from lucerne.—See A., 1939, III, 498.

Action of light on substances related to ergosterol. G. A. D. HASLEWOOD (Biochem. J., 1939, 33, 454—456).—In the oxidation of stigmasteryl acetate by CrO_3 , 6-keto-3:5-diacetoxy- Δ^{23} -sitostene, m.p. 189—190°, is obtained as a by-product together with 7-ketostigmasteryl acetate, new m.p. 184—185°. 7-Dehydrostigmasteryl (I), new m.p. 149—151° [from 7-benzoyloxy-stigmasteryl benzoate, m.p. 184—186° (lit. 156—158°), and boiling NPhMe_2 followed by hydrolysis ($\text{EtOH-COMe}_2\text{-2N-NaOH}$)], in $\text{EtOH-C}_6\text{H}_6$ (4:1), when exposed to sunlight in presence of eosin, yields a compound, m.p. 203—204°. 3-Hydroxy- $\Delta^{5:7}$ -choladienic acid (II), similarly isolated in EtOH , yields a compound, m.p. 238—239°. Irradiation of (I) and (II) yields products with vitamin-D activity of <25 I.U. per mg.

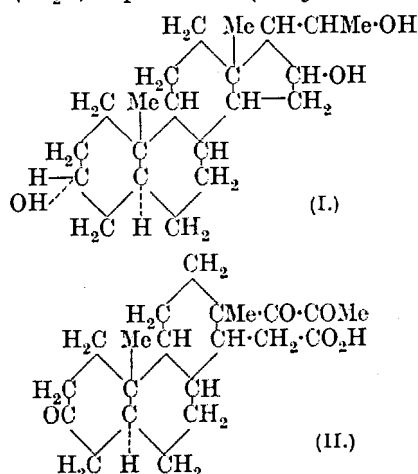
P. G. M.

Total synthesis of the sex hormone, equilenin. W. E. BACHMANN, W. COLE, and A. L. WILDS (J. Amer. Chem. Soc., 1939, 61, 974—975).—Condensation of 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene and $\text{Me}_2\text{C}_2\text{O}_4$ and elimination of CO gives *Me* 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthr-

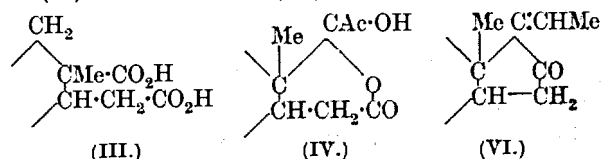
ene-2-carboxylate ($\sim 90\%$), the 2-Me derivative, m.p. 84.5—86°, of which with $\text{CH}_2\text{Br-CO}_2\text{Et}$ etc. gives *cis*-, m.p. 228—230°, and *trans*-2-carboxy-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthryl-1-acetic acid, m.p. 208—210°. The Arndt-Eistert procedure then converts the *trans*-acid into the corresponding 1-propionic acid, m.p. 101—102°, the Me_2 ester of which is cyclised by Na to a product, which by hydrolysis and decarboxylation gives *dl*-equilenin, m.p. 265—267°, resolved by way of the *l*-menthoxyacetate. No details are given.

R. S. C.

Sterols. LV. Structure of pregnanetriol-B. R. E. MARKER and E. L. WITTLE (J. Amer. Chem. Soc., 1939, 61, 855—860).—Pregnanetriol-B (A., 1938, II, 97, 277) is proved to be allopregnane-3(α):16:20-triol (I) (cf. Odell *et al.*, A., 1938, II, 442). $\text{CrO}_3\text{-AcOH}$ oxidises it to the acid (II), $\text{C}_{21}\text{H}_{30}\text{O}_5$, anhyd., an oil, and $+\text{H}_2\text{O}$, m.p. 95—98° (benzylthiuronium salt



m.p. 176°; dioxime, m.p. 183°), and a small amount of 3-keto Δ^2 alloboilanic acid (III), m.p. 260° (decomp.) [2:4-dinitrophenylhydrazones, m.p. 260°; anhydride, m.p. 224°; Me_2 ester, m.p. 135° (semicarbazone, m.p. 200°)]. (II) reacts with HIO_4 (proof of CO-CO), gives CHI_3 (proof of COMe), gives the Zimmermann test (proof of CO at C_{13}), and is yellow in solvents and when anhyd. (III) is present in the oxidation mixture as anhydride and is formed by way of (II) and the lactone (IV). Clemmensen reduction



of (III) gives Δ^2 alloboilanic acid, m.p. 260° (anhydride, m.p. 184°). Results previously reported (*loc. cit.*) are in part corr. *allo*Pregnane is the only hydrocarbon obtained from (I) by way of the chloride. Conversion of 4:20-diacetoxypregnan-3-one into pregnane-3:4:20-triol, followed by oxidation, gives an acid differing from (II). Partial hydrolysis (KOH-MeOH at room temp.) of the triacetate of (I) gives the 20-monoacetate, new m.p. 233—235°, oxidised by CrO_3 to (probably) 20-acetoxypregnan-3:16-dione (V),

m.p. 191°, which with KOH-aq. EtOH, NaHCO₃-MeOH, or HCl-EtOH is hydrolysed and dehydrated to the diketone (VI), C₂₁H₃₀O₂, m.p. 190—192° (*bis*-2 : 4-dinitrophenylhydrazones, red, m.p. 190°). Reduction of (VI) by Na-EtOH gives the saturated diol. C₂₁H₃₆O₂, m.p. 255° (*diacetate*, m.p. 140°), which with CrO₃ yields the saturated diketone, C₂₁H₃₂O₂, m.p. 128° (*bis*-2 : 4-dinitrophenylhydrazones, m.p. 245°). The "pyridazine" (Odell *et al.*) from (V) is a mixture of linear polymerides; a similar mixture is obtained from allopregnane-3 : 20-dione and N₂H₄. Na in xylene has little effect on (I), but in C₅H₁₁OH gives 3-β-OH-compounds (digitonide), including a diol, C₂₆H₄₆O₂, m.p. 209° (*diacetate*, m.p. 150°). R. S. C.

Mechanism of the Perkin reaction. III. Formation of cinnamic acid. D. A. BRODSKI (J. Gen. Chem. Russ., 1938, 8, 1534—1540).—Cinnamic acid is obtained from mixtures of PhCHO, AcOH, and KOAc at 170—280° (26 hr.). Ac₂O is thus not an essential constituent of the Perkin reaction, and acts essentially as a dehydrating agent. The results support Fittig's explanation of the reaction, viz., PhCHO + KOAc → OH·CHPh·CH₂·CO₂K → CHPh·CH·CO₂K + H₂O. R. T.

Condensations brought about by bases. V. Condensation of the anhydride with the aldehyde in the Perkin synthesis. VI. Mechanism of the Perkin synthesis. C. R. HAUSER and D. S. BRESLOW (J. Amer. Chem. Soc., 1939, 61, 786—792, 793—798; cf. A., 1938, II, 413).—V. The following facts support the view that the anhydride, and not the salt, condenses with the aldehyde in the Perkin reaction. When Ac₂O and Pr^oCO₂Na are heated at 180° or 100° (to establish equilibrium) and then treated with PhCHO, the ratio of CHPh·CH·CO₂H to CHPh·CET·CO₂H formed is 5 : 7—8 or 2 : 8—9, respectively. The same proportions are formed when (Pr^oCO₂)O and NaOAc are used. The ratio depends mainly on the amount of the anhydrides in the equilibrium mixture. PhCHO, Ac₂O, and CH₂Ph·CO₂Na (I) at 195° give mainly CHPh·CPh·CO₂H (II), owing to PhCHO condensing much faster with (CH₂Ph·CO)₂O (III) than with Ac₂O. When Ac₂O and (I) are first heated at 180° and then treated with PhCHO, only a little (II) is formed and much PhCHO is recovered; much CO(CH₂Ph)₂ is formed by self-condensation (during the preliminary heating) of (III). Contrary to Stuart (J.C.S., 1883, 43, 403), PhCHO, Ac₂O, and CH₂(CO₂Na)₂ do not react, unless AcOH is also present, which leads to formation of CH₂(CO₂H)₂ and thence of CHPh·CH(CO₂H)₂ or CHPh·CH·CO₂H. Ac₂O and CH₂(CO₂Na)₂ develop a colour at room temp. without evolving CO₂.

VI. The mechanism of the Perkin reaction is: PhCHO + (CH₂R·CO)₂O → OH·CHPh·CHR·CO·O·CO·CH₂R → CHPh·CR·CO·O·CO·CH₂R → CHPh·CR·CO₂H + CH₂R·CO₂H. The OH-anhydride and -acid are isolated in several cases. PhCHO, (Pr^oCO₂)O, and Pr^oCO₂Na in N₂ give Pr^oCO₂·CHPh·CMe₂·CO₂H and the mixed anhydride, hydrolysed to the OH-acid. Pr^oCO₂Et, converted by NaCPh₃ into its enolate and then kept with PhCHO for 20 min., gives 29.5% of OH·CHPh·CMe₂·CO₂Et; this is converted into PhCHO

and Pr^oCO·CMe₂·CO₂Et when kept with NaCPh₃, which accounts for the results of Müller (A., 1932, 56; 1935, 344). When EtOAc is treated first with NaCPh₃ and then for >1 min. with PhCHO, it gives OH·CHPh·CH₂·CO₂Et, hydrolysed to the acid, m.p. 92—93.5°. In presence of bases, CH₂(CO₂Et)₂ and PhCHO give CHPh·C(CO₂Et)₂ (IV); however, pure CHNa(CO₂Et)₂ and PhCHO in C₆H₆ give only a little (IV), the main reaction being that of Cannizzaro. In the absence of proton donors, (IV) cannot be formed; bases act by being proton donors, and, in their absence, (IV) is not formed until the proton-donating products of the Cannizzaro reaction have accumulated. The exact ionic mechanism is discussed. R. C. S.

Conversion of coumarin derivatives into o-methoxycinnamic acids. N. M. SHAH and R. C. SHAH (J. Univ. Bombay, 1938, 7, 213—215).—o-Methoxycinnamic acids are satisfactorily obtained by adding Me₂SO₄ and 20% KOH alternately to coumarin in hot COMe₂, even when prep. by methylation after hydrolysis fails. R. S. C.

Reaction of aromatic diazo-compounds with α,β-unsaturated carbonyl compounds. H. MEERWEIN, E. BÜCHNER, and K. VAN EMSTER (J. pr. Chem., 1939, [ii], 152, 237—266).—Interaction of the appropriate ArN₂Cl with coumarin and NaOAc in COMe₂ followed by aq. CuCl₂ yields 3-*p*-chlorophenyl-, 3-phenyl-, 3-β-naphthyl-, m.p. 170°, 3-*p*-nitrophenyl-, 3-*o*-nitrophenyl-, m.p. 172—173°, 3-*p*-anisyl-, m.p. 136.5—138.5°, 3-*p*-acetamidophenyl-, m.p. 249.5°, 3-*p*-sulphophenyl- (*Na* salt), and 3-*p*-carboxyphenyl-coumarin, m.p. 288—290°. Similarly, umbelliferone (I) and *p*-C₆H₄Cl·N₂Cl (II) give 7-hydroxy-3-*p*-chlorophenylcoumarin, m.p. 280—282°, but in aq. Na₂CO₃ the azo-dye, C₁₅H₉O₃N₂Cl, is formed. *p*-NO₂·C₆H₄·N₂Cl with CHPh·CH·CO₂H (III), NaOAc, and CuCl₂ in COMe₂ yields *p*-nitrostilbene and α-*p*-nitrophenylcinnamic acid. Similarly from (III) and the appropriate ArN₂Cl are obtained stilbene, *p*-methyl-, *p*-chloro-, 2 : 4-dichloro-, m.p. 77.5°, *o*-nitro-, and *p*-methoxy-stilbene, and *Na* stilbene-*p*-sulphonate, decomp. ~259°.

p-OH·C₆H₄·CH·CH·CO₂H with (II) in aq. CH₂Cl·CO₂Na gives 4-chloro-4'-hydroxystilbene, m.p. 185.5—186°; similarly, from *p*-chloro- and *p*-methoxy-cinnamic acids are formed 4 : 4'-dichloro- and 4-chloro-4'-methoxy-stilbene respectively. CHPh·CH·CN and (II) yield α-*p*-chlorophenylcinnamitrile, whilst (II) and Me cinnamate (IV) in aq. AcOH-C₅H₅N give Me β-chloro-β-phenyl-α-*p*-chlorophenylpropionate, m.p. 124—124.5°, which with NaOAc in AcOH at 140° yields Me α-*p*-chlorophenylcinnamate, m.p. 85.5° [free acid (V), m.p. 181.5°]. *p*-C₆H₄Cl·N₂Br and (IV) yield Me β-bromo-β-phenyl-α-*p*-chlorophenylpropionate, m.p. 123°. Crotonic acid and *p*-NO₂·C₆H₄·N₂Cl in COMe₂ with CuCl₂ and CH₂Cl·CO₂Na yield α-*p*-nitrophenylcrotonic acid, m.p. 173.5—174.5°, and 4 : 4'-dinitroazobenzene. 2 : 4 : 1-C₆H₃Cl₂·N₂Cl and Me crotonate give Me β-chloro-α-2 : 4-dichlorophenylbutyrate, b.p. 130—140°/0.1 mm., hydrolysed (cold EtOH-KOH) to the acid, m.p. 124.5—125°. With CPh·C·CO₂H, (II) gives Me β-chloro-α-*p*-chlorophenylcinnamate, b.p. 160—165°/0.1 mm., m.p. 63°. Me₂ fumarate and (II) form

Me_2 β -chloro- α -p-chlorophenylsuccinate (VI), m.p. 79° [hot EtOH-KOH then gives p-chlorophenylfumaric acid (VII), m.p. 222°], and an oil which on hydrolysis gives (VII). Distillation of (VII) with chlorocymene-sulphonic acid gives p-chlorophenylmaleic anhydride, (VIII), m.p. 146°, hydrolysed by H_2O to the acid. (VIII) is slowly converted into (VII) by boiling 2N-NaOH. Similarly, (II) and Me_2 maleate give (VI) and (VII), but no (VIII); the primary reaction product with boiling 2N-NaOH affords (VII) and (VIII). $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ and (II) give α -p-chlorophenylcinnamaldehyde, m.p. 85–86° [oxidised by Ag_2O in C_6H_6 to (V)], and an isomeride, m.p. 128°. Reaction mechanisms are discussed. $\text{COMe}\cdot\text{CH}_2\text{Hal}$ is produced in considerable amount from the COMe_2 used as solvent; negative substituents in the ArN_2Hal favour its production. (II) and SO_2 in boiling aq. CuCl_2 give ~80% of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Cl}$; in presence of NaOAc (no CuCl_2), $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Cl}\cdot p$ is formed. J. D. R.

4-Aminocyclohexylacetic acid. E. FERBER and H. BENDIX (Ber., 1939, 72, [B], 839–848).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ is converted by boiling ~95% EtOH saturated with HCl into $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 65–66°, reduced (PtO_2 in 96% EtOH) to $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I), m.p. 49–50°. $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is hydrogenated at 60°/3 atm. (PtO_2 in AcOH) to 77.5% of cis- (II), m.p. 185–187°, and 22.5% of trans-4-acetamidocyclohexylacetic acid, m.p. 235° (Et esters, m.p. 60–62° and 115–116° respectively). (I) is converted by Na_2CO_3 and Me_2SO_4 in H_2O into Et p-methylaminophenylacetate (III), b.p. 130°/2 mm. 297° (slight decomp.)/739 mm. [hydrochloride, m.p. 217°; NO-derivative, m.p. 37°; free acid, an oil (NO-derivative, m.p. 126°)]. Hydrogenation (PtO_2 , 96% EtOH, conc. HCl at 50–55°/3 atm.) of (III) yields an ester mixture, b.p. 127°/10 mm., benzoylated to Et cis- (82%), m.p. 83–87°, and trans- (18%), m.p. 147–148°, 4-methylbenzamidocyclohexylacetate, from which the corresponding acids, m.p. 186–188° and 235–236°, respectively are derived. Condensation of EtOAc with Et 2-methylcinchoninate by NaOEt yields Et 2-methyl-4-quinolylacetate, hydrolysed by boiling 25% H_2SO_4 into CO_2 and 4-acetyl-2-methylquinoline, m.p. 68–69° [hydrochloride, m.p. 153°; picrate, m.p. 177–178°, and its p-nitrophenylhydrazone, m.p. 257° (decomp.)]. Et cis-4-acetamidocyclohexylacetate and Et quininate yield the non-cryst. Et 6-methoxy-4-quinolyl-4'-acetamidocyclohexylacetate, hydrolysed to 6-methoxy-4-p-acetamidocyclohexylacetylquinoline, an oil [picrate, m.p. 170°, and its p-nitrophenylhydrazone, m.p. 252° (decomp.)].

H. W.

Reactions of etherates of stannic chloride and titanium tetrachloride. III. Reaction of dioxanates and tetrahydrofuranates of stannic chloride and titanium tetrachloride with acid chlorides. J. L. GOLDFARB and L. M. SMORGONSKI (J. Gen. Chem. Russ., 1938, 8, 1516–1522).—Dioxan, BzCl , and TiCl_4 (10 hr. at 150–180°) yield β -chloroethyl benzoate (I), b.p. 263°, whilst with SnCl_4 , $(\text{CH}_2\cdot\text{OBz})_2$ (II) is also obtained; (I), SnCl_4 , and BzCl also give (II). With AcCl and SnCl_4 the sole

product is $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$. Tetrahydrofuran, BzCl , and SnCl_4 (12 hr. at 160–200°) yield $(\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz})_2$ and δ -chlorobutyl benzoate, b.p. 144–145°/55 mm.; the product with AcCl is δ -chlorobutyl acetate, b.p. 187–190°, whilst with SOCl_2 or HCl $\alpha\delta$ -dichlorobutane is obtained. R. T.

Preparation of o-tolu-, o-chlorobenz-, and o-anis-arylamides. N. W. HIRWE, G. V. JADHAV, and D. R. SUKHTANKAR (J. Univ. Bombay, 1938, 7, 216–217).—The appropriate acid (3 mols.), amine (3 mols.), and PCl_3 (1 mol.) at 120° give good yields of o-tolu-anilide, m.p. 128° (lit. 125°), -o-, m.p. 140°, -m-, m.p. 144°, and -p-toluidide, m.p. 142° (lit. 144°), and -p-chloroanilide, m.p. 133°, o-chlorobenz-o-, m.p. 100°, -m-, m.p. 129–130°, and -p-chloroanilide, m.p. 121°, and o-anis-anilide, m.p. 69° (lit. 62°), and -o-anisidide, m.p. 100°. R. S. C.

Interaction of sulphuryl chloride with aryl-amides of aromatic acids. I. G. V. JADHAV and D. R. SUKHTANKAR (J. Indian Chem. Soc., 1938, 15, 649–652).—The following products are obtained from amides and SO_2Cl_2 in C_6H_6 : from NHPhBz , benz-p-chloro-, m.p. 190–191°, and -2:4-dichloro-, m.p. 115–116° (also obtained from o- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHBz}$), and from m- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHBz}$, benz-3:4-dichloro-anilide, m.p. 143–144°; benz-o-, -m-, and -p-toluidide give respectively benz-5-chloro-o-, m.p. 162–163°, -6-chloro-, m.p. 116–118°, and -2:6-, m.p. 147–148°, and -4:6-dichloro-m-, m.p. 111–112°, and -3-chloro-, m.p. 139°, and -3:5-dichloro-p-toluidide, m.p. 114–115°; from benz-p-anisidide, benz-2:5-dichloro-p-anisidide, m.p. 136–137°; from benz-p-phenetidine, benz-2-chloro-, m.p. 171–172°, and -2:5-dichloro-p-phenetidine, m.p. 144–145°; from benz- α - and - β -naphthylamide, respectively, benz-4-chloro-, m.p. 226°, and -2:4-dichloro- α -, m.p. 212–213°, and -1-chloro- β -naphthylamide, m.p. 171°; from benz-o-nitroanilide, benz-4-chloro-2-nitroanilide, m.p. 130°. E. W. W.

Separated auxo-enoid systems. V. Coloration of nitrobenzoyl derivatives of aromatic amines. V. A. IZMAILSKI and E. A. SMIRNOV (J. Gen. Chem. Russ., 1938, 8, 1730–1741).—Intense red or yellow colorations develop when the systems $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ or $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ -m- or -p- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ (I) and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$ -(I) are fused (100–150°) or heated in org. solvents; these colorations disappear when the systems are cooled, and are ascribed to formation of unstable 1:1 compounds, the structure of which is discussed. R. T.

Preparation of anisylidene-p-aminobenzo-nitrile. B. M. BOGOSLOVSKI (J. Gen. Chem. Russ., 1938, 8, 1784–1785).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ is converted (Sandmeyer) into $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (68% yield), from which $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ (I) (anisylidene derivative) is obtained (66% yield) by hydrolysis with 20% H_2SO_4 (30 min. at the b.p.). This synthesis gives a purer product, in higher yield, than do other syntheses of (I). R. T.

Mono- and di-methoxyanthranilic acids and their derivatives. V. M. RODIONOV and A. M. FEDOROVA (Bull. Soc. chim., 1939, [v], 6, 478—

486).—4-Hydroxyanthranilic acid (I) [prepared thus: 4-nitro- \rightarrow 4-amino- \rightarrow 4-hydroxy-phthalimide \rightarrow (I)] with $C_6H_4Me \cdot SO_3 \cdot NPhMe_3$ (pretreated with $EtOH-NaOEt$) at 115–120°, followed by $MeOH-H_2SO_4$, yields *Me* 4-methoxyanthranilate, m.p. 116–118° [also prepared from the *Me* ester, m.p. 154–155°, of (I), dil. aq. KOH , and Me_2SO_4] [*N-Me* derivative (prep. by $p-C_6H_4Me \cdot SO_3Me$), m.p. 81–83°]. 3:4-Dimethoxyanthranilic acid (II) (A., 1934, 1106) [*Me* ester, m.p. 69–70° (*N-Me* derivative *hydrochloride*)] does not react with $PhCHO$, but with Ac_2O yields the corresponding *N*-acetyldimethoxyanthranil, m.p. 165–168° [which when cryst. from $AcOH$ gives the *N-Ac* derivative, m.p. 193–195°, of (II)], converted by aq. NH_3 into ~50% of 7:8-dimethoxy-2-methylquinazoline, m.p. 223–224° (*hydrochloride*, m.p. 226–228°). 5:6-Dimethoxyanthranilic acid (III) (*loc. cit.*) [*Me* ester, m.p. 49–50° (*hydrochloride*, m.p. 185–186°; *N-Me* derivative, m.p. 61–62°, and its *hydrochloride*, m.p. 173–174); *CHPh* derivative, m.p. 145–150°] with Ac_2O yields the corresponding *N*-acetyldimethoxyanthranil, m.p. 114–115° [converted by $AcOH$ into the *N-Ac* derivative, m.p. 179–180°, of (III)], which does not give a quinazoline derivative with aq. NH_3 but yields 5:6-dimethoxyacetanthranilamide, m.p. 236–237°.
A. LI.

Chloral-amides. V. Reactivity of hydroxyl groups in chlorosalicyl- $\beta\beta\beta$ -trichloro- α -hydroxyethylamides. II. N. W. HIRWE and K. N. RANA (J. Univ. Bombay, 1938, 7, 174–177; cf. A., 1938, II, 190).—3-Chloro-, 5-chloro-, and 3:5-dichlorosalicyl- $\beta\beta\beta$ -trichloro- α -hydroxyethylamide (I) with Ac_2O and a little H_2SO_4 or Me_2SO_4 and 10% $NaOH$ give the *Ac* derivatives, m.p. 95–97°, 143–144°, and 142–144°, or *Me* ethers, m.p. 84–85°, (II) 131–132°, and (III) 102–103°, respectively. 2:3:1- and 2:3:5:1- $OMe \cdot C_6H_3Cl_3 \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3$ and 2:3:5:1- $OMe \cdot C_6H_3Cl_3 \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3$ with $Ac_2O-H_2SO_4$ or Me_2SO_4-NaOH give the *Ac* derivatives, m.p. 93–94°, 124–125°, and 153–154°, and the ethers, —, (II), and (III), respectively, but $Ac_2O-10\%$ $NaOH$ gives *bis*- $\beta\beta\beta$ -trichloro- α -5-chloro-, m.p. 109–110°, and -3:5-dichloro-2-methoxybenzamidoethyl ether, m.p. 98–100°. With $BzCl-10\%$ $NaOH$ (I) gives its *Bz* derivative, m.p. 110–112° (decomp.).
R. S. C.

Fluorenones and diphenic acids. VI. Ring cleavage of 2-chloro-, 2-hydroxy-, 2-amino-, and 2-sulpho-fluorenones by potassium hydroxide in diphenyl ether. E. H. HUNTRESS and (MISS) M. K. SEIKEL (J. Amer. Chem. Soc., 1939, 61, 816–822; cf. A., 1936, 1377).—Alkaline fission of fluorenones is best effected by ~15 mols. of KOH in Ph_2O at 180–200°. Fluorenone thus gives nearly 100% of $o-C_6H_4Ph \cdot CO_2H$, whereas with hot 5*N*- $KOH-MeOH$ it gives 95% of fluorenol (I), with saturated $KOH-EtOH$ a trace of fluorenylacetic acid (II), with 1-5*N*- $KOH-(CH_3OH)_2$ at 170–180° 60–70% of (I) and 13% of (II), and with 20*N*-aq. KOH it is unchanged. In Ph_2O 2-chlorofluorenone (III) (modified prep. from 2-aminofluorenone, m.p. 156–157°), m.p. 120.5–122°, yields mainly 4'-chlorodiphenyl-2-carboxylic acid (IV), m.p. 166.5–166°, the structure of which is proved as follows. With cold H_2SO_4 it gives (III). With PCl_5 it gives a chloride and thence successively the *amide*, m.p. 165°, (by $NaOBr$) 4'-chloro-2-aminodiphenyl, m.p. 47–48° (lit. 52° and 71°) (*Ac* derivative, m.p. 121.5–122.5°), and (by $KMnO_4$) $p-C_6H_4Cl \cdot CO_2H$. 1:5:2- $C_6H_3MeCl \cdot N_2 \cdot ONa$ and C_6H_6 give 4-chloro-2-methyldiphenyl, b.p. 160–162°/19 mm., converted by $KMnO_4$ into 4-chlorodiphenyl-2-carboxylic acid, m.p. 157–158° [depresses the m.p. of (IV)]; with cold H_2SO_4 also gives (III)], but by CrO_3-AcOH into 1:5:2- $C_6H_3MeCl \cdot CO_2H$. 2-Hydroxyfluorenone and KOH in Ph_2O at 180° give >50% of 4-hydroxydiphenyl-2-carboxylic acid (V), m.p. 202–202.5° (no $FeCl_3$ colour), cyclised to the ketone by H_2SO_4 ; acids described as (V), but obtained by alkali fusion of sulphonic acids, were mixtures. 2-Aminofluorenone and KOH in Ph_2O at 160–170° give a mixture, which after diazotisation yielded 4'-hydroxydiphenyl-2-carboxylic acid (VI), although the isomeric acid was probably also formed. Fluorene-2-sulphonic acid and KOH in Ph_2O at 180° give 40% of (VI). *K* fluorenone-2-sulphonate and KOH in Ph_2O give rapidly 2- and 2'-carboxydiphenyl-4-sulphonates and much more slowly (VI) therefrom.
R. S. C.

Kolbe's electro-synthesis in the case of an aromatic acid. F. FICHTER and H. STENZL (Rocz. Chem., 1938, 18, 510–514).—Electrolysis of *K* hydrindene-2-carboxylate in $MeOH$ yields 2:2'-dihydrindyl, m.p. 165–166° (*Br*₂-derivative, decomp. 300°) (cf. A., 1939, II, 214).
R. T.

Derivatives of α - and β -naphthoic acids. A. WAHL, M. L. GOEDKOOP, and E. HEBERLEIN (Bull. Soc. chim., 1939, [v], 6, 533–548).—Largely a more detailed account of work previously reviewed (A., 1938, II, 143, 364). Methods of preparing naphthoic acids are discussed. Et α -naphthoylacetate (I) with NH_2OH (salt) in aq. $EtOH$ yields α -naphthyl *Me ketoxime*, m.p. 142°, but with NH_2OH in neutral solution gives 3- α -naphthyl-5-isooxazolone, m.p. 193°. (I) with PhN_2Cl , $p-NO_2 \cdot C_6H_4 \cdot N_2Cl$, and diazotised 1:4- $NH_2 \cdot C_{10}H_6 \cdot SO_3H$ in aq. $EtOH$ yields respectively *Et benzeneazo*-, *p-nitrobenzeneazo*-, m.p. 137.5°, and 4-sulpho-1-naphthaleneazo- α -naphthoylacetate. 3- β -Naphthyl-5-isooxazolone, m.p. 159°, with isatin, 7-chloroisatin, and 5:7-dimethylisatin chlorides in C_6H_6 gives 2-indoxylidene-3- β -naphthyl-5-isooxazolone, m.p. 250°, and its 7'-*Cl*-, m.p. 214–226°, and 5':7'-*Me*₂ derivative, m.p. 190–191°, respectively. α -Naphthoylacet-anilide, m.p. 119–120°, and *o*-aniside, m.p. 124°, are described.
A. LI.

Constitution of α -sorigenin. Z. NIKUNI (J. Agric. Chem. Soc. Japan, 1939, 15, 283–290).— α -Sorigenin (I), $C_{13}H_{10}O_5$, m.p. 227–229°, contains 2 OH, 1 OMe, and a lactone ring. Distillation of diacetyl- α -sorigenin with Zn in H_2 yields a product, $C_{12}H_{12}$, m.p. 90–96°, probably 2:3- $C_{10}H_6Me_2$. (I) is probably the lactone of a dihydroxymethoxy-3-hydroxymethyl-2-naphthoic acid.
J. N. A.

Syntheses in the phenanthrene series. II. R. GREWE (Ber., 1939, 72, [B], 785–790).— α -2-Carboxymethylenecyclohexyl- β -phenylpropionic acid, m.p. 217° (A., 1939, II, 159), is decarboxylated by Cu

powder in quinoline at 200° to α -2-methylenecyclohexyl- β -phenylpropionic acid (I), m.p. 130° (with small amounts of an isomeric, m.p. 91°), converted by O₃ into CH₂O and α -2-ketocyclohexyl- β -phenylpropionic acid (II). Cyclisation of (I) by syrupy H₃PO₄ at 130° gives two 12-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-10-carboxylic acids, m.p. 142° (III) and 178° (IV); (III) with Pd-sponge at >300° gives phenanthrene and a mixture of (III) and (IV). MgMeI in Et₂O converts (II) into α -2-hydroxy-2-methylcyclohexyl- β -phenylpropionic acid, m.p. 121° (decomp.), which readily passes into the corresponding lactone, b.p. 167°/0.2 mm. This is cyclised by syrupy H₃PO₄ at 50° to (III) and (IV), and is transformed by P₂O₅ at 140° into 1-methylhexahydrophenanthrene, b.p. 124°/0.3 mm., dehydrogenated (Pd at 240°) to 1-methylphenanthrene. H. W.

Hydroxy- and methoxy-phenylsuccinic acids. K. P. DAVE and K. S. NARGUND (J. Univ. Bombay, 1938, 7, 196—202).—The following are obtained from ArCHO and CN·CH₂·CO₂Na by way of CHAR·C(CN)·CO₂H, its ester, and CN·CHAR·CH(CN)·CO₂H, hydrolysed to CO₂H·CHAR·CH₂·CO₂H by conc. HCl. α -Cyano- β -o-, m.p. 210° (Et ester, m.p. 75°), and -m-anisyl-, m.p. 170° (Me, m.p. 76°, and Et ester, m.p. 56°), -m-, m.p. 229° (Me, m.p. 153°, and Et ester, m.p. 98°), and -p-hydroxyphenyl-acrylic acid, m.p. 244° (Me, m.p. 211°, and Et ester, cryst.); o- (I), m.p. 172° (lit. 150°) (Et, m.p. 75°, and Me ester, m.p. 98—99°), m-, m.p. 124° (dianilide, m.p. 145°; di-p-toluidide, m.p. 178°), and p-hydroxyphenylsuccinic acid (II) (25% yield), m.p. 164° (Me ester, b.p. 150—160°/20 mm.; dianilide, m.p. 183°); o- [prep. from (I) or from o-OMe·C₆H₄·CHO, using 25% HCl for hydrolysis of the dinitrile], m.p. 178° (Me, b.p. 146°/17 mm., and Et ester, b.p. 165°/12 mm.; anhydride, m.p. 130°; anilide, m.p. 170°; p-toluidide, m.p. 170°; dianilide, m.p. 157°; di-p-toluidide, m.p. 126°), and m-anisylsuccinic acid, m.p. 176° (Me, m.p. 81°, and Et ester, b.p. 185°/7 mm.; anilide, m.p. 161°; p-toluidide, m.p. 150°; dianilide, m.p. 110°; di-p-toluidide, m.p. 116°; anhydride, m.p. 57°). CO₂H·CHPh·CH₂·CO₂H and HNO₃ (d 1.42) give only the p-NO₂-derivative, which with Sn-HCl gives a good yield of the NH₂-acid, m.p. 226°, and thence (II), which is, however, best obtained from p-OMe·C₆H₄·CH(CO₂H)·CH₂·CO₂H by HBr.

R. S. C.

Synthesis and derivatives of α - γ -diphenylglutaconic acid. N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1938, 7, 203—204).—CHCl₃, CH₂Ph·CO₂Et, and NaOEt·EtOH give Et₂ α - γ -diphenylglutaconate, m.p. 140°, hydrolysed by 10% NaOH to the acid, m.p. 230° (Ag₂ salt; Me₂ ester, m.p. 169—170°; anhydride, m.p. 120°; dianilide, m.p. 234°), which is reduced by Na-Hg to CH₂(CHPh·CO₂H)₂, new m.p. 189—190°. CHCl₃ and CHBr₃ give unsatisfactory results.

R. S. C.

Action of formaldehyde on anæsthesine. H. LECOQ (Bull. Soc. chim. Belg., 1939, 48, 71—76).—The ppt. obtained from p-NH₂·C₆H₄·CO₂Et and CH₂O in very dil. HCl is di-p-carbethoxyanilinomethane, m.p. 185.5°. It gives reactions of CH₂O only after hydro-

lysis, but gives the morphine-H₂SO₄ reaction for CH₂O if crystallised from EtOH or C₆H₆ (trace of free CH₂O).

R. S. C.

Production of phthalic anhydride.—See B., 1939, 463.

Condensation product of methyl o-aldehydobenzoate and malonic acid. S. HANAI (Bull. Inst. Phys. Chem. Res. Japan, 1938, 17, 1236—1240).—o-CHO·C₆H₄·CO₂Me and CH₂(CO₂H)₂ yield a compound, m.p. 311—312°, a decomp. product of which is o-CO₂H·C₆H₄·[CH₂]₂·CO₂H. Dipthalide ether melts at 235—236°.

A. LI.

Degradation of deoxycholic acid to bisnorcholic acid. J. SAWLEWICZ (Rocz. Chem., 1938, 13, 755—761).—Me deoxycholate in C₆H₆ and MgMeCl are heated at 100° for 5 hr., and the product is added to aq. NH₄Cl at 0°, to yield 3:12-dihydroxynorcholanyldimethylcarbinol, an oil [Ac₃ derivative (I), m.p. 111—112.5°]; diphenyl-3:12-dihydroxynorcholanyldimethylcarbinol, m.p. 115—119°, prepared analogously, gives with Ac₂O in C₆H₅N α -diphenyl- β -3:12-diacetoxynorcholanylethylene. This, or (I), is oxidised (CrO₃ in AcOH) to 3:12-diacetylnordeoxycholic acid, m.p. 207.5—209.5° (Me ester, m.p. 157—159°), hydrolysed (KOH in MeOH) to nordeoxycholic acid, the Me ester, m.p. 164—165.5°, of which is converted (Grignard reaction) into 3:12-dihydroxybisnorcholanyldimethylcarbinol, m.p. 211—212.5° [the acetate is oxidised (CrO₃) to 3:12-diacetoxylbisnordeoxycholic acid, m.p. 185—186°, hydrolysed to bisnordeoxycholic acid (Me ester, m.p. 167—168.5°)].

R. T.

Isomerisation of α - β -oxido- α -phenyl- β -vinylbutane into α -phenyl- α -vinylbutaldehyde and dehalogenation of the corresponding iodohydrin to δ -keto- γ -phenyl- Δ^6 -hexene. Y. DEUX (Compt. rend., 1939, 208, 1090—1092; cf. A., 1938, II, 231).—OH·CHPr^a·SO₃Na with PhCHO in presence of KOH gives β -phenyl- α -ethylacraldehyde, b.p. 126—128°/14 mm. (oxime, m.p. 108—109°; semicarbazone, m.p. 216—217°), which with MgMeI affords β -hydroxy- γ -benzylidenepentane, dehydrated to α -phenyl- β -ethyl- Δ^6 -butadiene (I), b.p. 110—111°/14 mm., which with HOCl, followed by KOH in Et₂O, affords α - β -oxido- α -phenyl- β -vinylbutane (II), b.p. 114—115°/14 mm. The vapour of (II) at 250—300°/14 mm. affords α -phenyl- α -vinylbutaldehyde (III), b.p. 115—116°/14 mm. (semicarbazone, m.p. 160°), reduced (H₂—Raney Ni) to CPhEt₂·CHO. (I) with I and HgO in Et₂O·H₂O affords an iodohydrin, converted by AgNO₃ into δ -keto- γ -phenyl- Δ^6 -hexene, b.p. 120°/14 mm. (semicarbazone, m.p. 148°), which when heated with EtOH·KOH gives EtCO₂H and CH₂Ph·CH·CH₂. The formation of (III) indicates that the affinity of Ph is < that of Et and CH₂CH₂.

J. L. D.

Aldehydes and hydroxyaldehydes of the polymethylene series. IX. Transformations of cyclopropylformaldehyde. E. D. VENUS-DANILOVA and V. F. KAZIMIROVA (J. Gen. Chem. Russ., 1938, 8, 1438—1446).—cycloPropanal (I) and 92% H₂SO₄ at 0° yield OH·CHET·CHO, whilst with 60% H₂SO₄ at 120—130° the product is COMe·CHMe·OH. With Br in CS₂ (I) gives CH₂Br·CH₂·CHBr·CO₂H.

R. T.

Synthesis of heliotropin [3:4-methylenedioxybenzaldehyde] from pyrocatechol. P. P. SCHORIGIN, A. A. SIMANOVSKAJA, and A. V. BOGDANOVA (J. Gen. Chem. Russ., 1938, 8, 975—980).—Aq. CH_2O and Al turnings are added to $o\text{-C}_6\text{H}_3(\text{OH})_2$ (I) and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$ in aq. HCl at 3—5°, and the mixture is heated, to yield 3:4:1-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$ (32—35% yield). (I), CH_2Cl_2 , and NaOH heated in 90% EtOH for 17 hr. at 110—115° give $o\text{-C}_6\text{H}_3\text{O}_2\text{CH}_2$ (23—45% yield), which with CH_2O in presence of ZnCl_2 and HCl at 10—15° affords piperonyl chloride (II) in 70—78% yield [*di*-(3:4-methylenedioxyphenyl)methane, m.p. 147°, is obtained as a by-product]. (II) and $(\text{CH}_3)_6\text{N}_4$ in 60% EtOH heated (1—2 hr. at the b.p.) give heliotropin (70—80% yield). R. T.

Condensation product of vanillin and phloroglucinol. R. GIULIANO (Annali Chim. Appl., 1939, 29, 86—88).—The “phloroglucinolvanillein” of Etti (A., 1883, 61) is a condensation product of phloroglucinol (1 mol.) and vanillin (1 mol.). F. O. H.

Dicinnamoylmethane series. I. Synthesis of three isomeric dinitro-derivatives. W. LAMPE and Z. MACIEREWICZ (Rocz. Chem., 1938, 18, 668—679).— $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ and $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$ (I) are condensed, and the product is heated, to yield *Et o-nitrodicinnamoylacetate* (II), m.p. 119—120°, converted by autoclaving into *o-nitrodicinnamoylmethane*, m.p. 156.5—157.5°, and by heating with 60% AcOH into *Et o-nitrocinnamoylacetate*, m.p. 70°, an Et_2O solution of which with (I) and MgMeI yields *Et di-o-nitrocinnamoylacetate*, m.p. 181°, autoclaved as above, to yield *di-o-nitrocinnamoylmethane*, m.p. 210°. $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ (III) and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$ afford *Et m-nitrocinnamoylacetate*, m.p. 116°, converted by hot AcOH into *Et m-nitrocinnamoylacetate*, m.p. 88—89°, from which *Et di-m-nitrocinnamoylacetate*, m.p. 208°, and 3:3'-*di-m-nitrocinnamoylmethane* are prepared as above. *Et p-nitrocinnamoylacetate*, m.p. 118° [from (III) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COCl}$], autoclaved with H_2O yields *p-nitrocinnamoylmethane*, m.p. 154—155° (decomp.). *Et p-nitrodicinnamoylacetate*, m.p. 188.5—189.5°, is prepared analogously to (II), and similarly yields *p-nitrodicinnamoylmethane*, m.p. 185°, *Et p-nitrocinnamoylacetate*, m.p. 110—111° (decomp.), *Et di-p-nitrocinnamoylacetate*, m.p. 196° (decomp.), and *di-p-nitrocinnamoylmethane*, m.p. 254—256°. 5-Nitrosalicylaldehyde and $\text{CH}_2(\text{CO}_2\text{Et})_2$ in presence of piperidine (90 min. at 100°) afford *Et 6-nitrocoumarin-3-carboxylate*, m.p. 198—199.5°, hydrolysed (10% NaOH) to the acid, m.p. 234.5°, the chloride, m.p. 171—172°, of which with cinnamoylacetone yields 6-nitro-3-cinnamoylacylcoumarin, m.p. 264—265° (decomp.). R. T.

Synthesis of hydroxy-derivatives of dicinnamoylmethane. M. TREKNERÓWNA (Rocz. Chem., 1938, 18, 830—839).—*Et o-carbomethoxyoxycinnamoylacetate* with boiling aq. AcOH yields *Et o-carbomethoxyoxycinnamoylacetate*, the Cu salt, m.p. 209°, of which with MgEtBr and *o-carbomethoxyoxycinnamoyl chloride* gives *Et di-o-carbomethoxyoxycinnamoylacetate*, m.p. 130—132°; this is autoclaved, to yield *di-o-carbomethoxyoxycinnamoylmethane*, m.p. 123—

125°, hydrolysed ($\text{NaOH}\cdot\text{COMe}_2$) to *di-o-hydroxycinnamoylmethane*, m.p. 170°. *o-Hydroxy-*, m.p. 165—170° (decomp.), and 2:4:2':4'-*tetrahydroxy-dicinnamoylmethane*, decomp. 123—125°, were prepared analogously. The following intermediates were obtained: *Et 2-carbomethoxy-*, m.p. 121—123°, and 2:4:2':4'-*tetracarbomethoxy-oxycinnamoylacetate*, m.p. 155°, *Et 2:4-dicarbomethoxyoxycinnamoylacetate*, m.p. 74° (Cu salt, m.p. 190°), and 2:4:2':4'-*tetracarbomethoxyoxycinnamoylmethane*, m.p. 147°. R. T.

Photochemical decomposition of aromatic ketones: the phenyl radical. H. H. GLAZEBROOK and T. G. PEARSON (J.C.S., 1939, 589—593).—The products of photochemical decomp. of COPhMe react with Te giving Ph_2Te , Me_2Te , and PhMeTe , b.p. 118—122°/22 mm. (1:1 compounds with HgCl_2 , m.p. 132°, HgBr_2 , m.p. 124—125°, and HgI_2 , m.p. 89—90°) (synthesised by treating a solid solution of I and Te with MgMeI and MgPhI in Et_2O), but in the absence of Te, Ph_2 , Bz_2 , and (?) $(\text{CH}_2\text{Bz})_2$ are formed. These results indicate the formation of Ph, Me, Bz, and (possibly) $\text{COPh}\cdot\text{CH}_2\cdot$ radicals. Similarly COPh_2 yields radicals (?) Ph which remove a Te mirror, the product in absence of Te being Ph_2 . A. LI.

Catalytic transformations of ketones. Isomerisation of phenyl *sec*-butyl ketone. T. E. ZALESKAJA (J. Gen. Chem. Russ., 1938, 8, 1589—1593).— $\text{COPh}\cdot\text{CHMeEt}$ (semicarbazone, m.p. 165°) heated with ZnCl_2 at 320° yields $\text{COMe}\cdot\text{CHPhEt}$. R. T.

Anomalous reactions of α -bromoketones. T. I. TEMNIKOVA (J. Gen. Chem. Russ., 1938, 8, 1022—1023).— $\text{COMe}\cdot\text{CHPhBr}$ and KOAc in EtOH yield chiefly $\text{COPh}\cdot\text{CHMe}\cdot\text{OAc}$ (I), together with some $\text{COMe}\cdot\text{CHPh}\cdot\text{OAc}$; with KOBz the chief product is $\text{COMe}\cdot\text{CHPh}\cdot\text{OBz}$, together with $\text{COPh}\cdot\text{CHMe}\cdot\text{OBz}$ (II). $\text{COPh}\cdot\text{CHMeBr}$ (III) and KOAc yield (I), which with MgMeBr affords β -phenylbutane- β -*g*-diol, b.p. 153—154.5°/17 mm. (III) and KOBz yield (II). R. T.

Preparation of polyhydroxychalkones. E. F. KURTH (J. Amer. Chem. Soc., 1939, 61, 861—862).—Addition of 3:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$ (I) and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ in a little EtOH to 60% aq. KOH in absence of air at $\sim 0^\circ$ and then keeping at room temp. for 3 days gives 46% of 3:4:2'-*trihydroxychalkone* [*o-hydroxyphenyl* 3:4-*dihydroxystyryl ketone*], m.p. 185—186° (*triacetate*, m.p. 112—113°), converted by a little H_2SO_4 in 50% aq. EtOH into 3':4'-*dihydroxyflavanone*, m.p. 188° (*diacetate*, m.p. 139°). 2:3:4-(OH) $_3\text{C}_6\text{H}_2\cdot\text{COMe}$, (I), and KOH give similarly 3:4:2':3':4'-*pentahydroxychalkone*, m.p. 249° (lit. 233°). R. S. C.

Chalkones. Reactivity of chalkone oxides. S. G. DEV and T. S. WHEELER (J. Univ. Bombay, 1938, 7, 205—212).—6-Substituents reduce the yields of glycollic acids obtained by alkali from 3:4-methylenedioxy-styryl ketone oxides. Other reactions of the oxides are described. 6-Chloropiperonal and COPhMe in 10% NaOH give *Ph 6-chloro-3:4-methylenedioxy-styryl ketone* (I), m.p. 136°, which with H_2O_2 and a little aq. NaOH in $\text{COMe}_2\text{-EtOH}$ at room temp. gives the oxide (II), m.p. 103—104°. With N_2H_4 in EtOH (II) gives the *hydrazone*, m.p. 179° (gives no

NO-derivative), converted by NaOEt-EtOH into 3-phenyl-5-6'-chloro-3':4'-methylenedioxyphenylpyrazole, m.p. 171°. With NHPH-NH₂ in warm AcOH (I) gives the phenylhydrazone, which in boiling AcOH affords 1:3-diphenyl-5-6'-chloro-3':4'-methylenedioxyphenyl-4:5-dihydropyrazole, m.p. 156°, oxidised by AgNO₃ in aq. EtOH to 1:3-diphenyl-5-6'-chloro-3':4'-methylenedioxyphenylpyrazole, m.p. 149—150° [also obtained from (II) by NHPH-NH₂ in AcOH at 100°]. With H₂SO₄ in hot MeOH or EtOH (II) gives *Ph* α -hydroxy- β -methoxy-, m.p. 169°, and β -ethoxy- β -6-chloro-3:4-methylenedioxyphenylethyl ketone, m.p. 134—138°, respectively. With hot NaOH-EtOH (1 min.) (II) gives *Ph* 6-chloro-3:4-methylenedioxybenzyl diketone, m.p. 157—158° (quinoxaline derivative, m.p. 114°), but heating for 4 hr. gives 20% of α -hydroxy- α -phenyl- β -6-chloro-3:4-methylenedioxyphenylpropionic acid, m.p. 157°. With HCO₂H or AcOH at 100° (II) yields *Ph* α -hydroxy- β -formoxy-, m.p. 170°, and β -acetoxy- β -6-chloro-3:4-methylenedioxyphenylethyl ketone, m.p. 155—156°, respectively, but H₂SO₄-HCO₂H affords *Ph* $\alpha\beta$ -diformoxy- β -6-chloro-3:4-methylenedioxyphenylethyl ketone, m.p. 145—146°. 3:4:6:1-(CH₂O)₂C₆H₂Br-CH₂-COPh yields similarly the oxide, m.p. 99—100° (hydrazone, m.p. 182—183°), 3-phenyl-5-6'-bromo-3':4'-methylenedioxyphenylpyrazole, m.p. 158—159°, 1:3-diphenyl-5-6'-bromo-3':4'-methylenedioxyphenylpyrazole, m.p. 149—150°, and 4:5-dihydropyrazole, m.p. 165—167°, *Ph* α -hydroxy- β -methoxy-, m.p. 165°, and β -ethoxy- β -6-bromo-3:4-methylenedioxyphenylethyl ketone, m.p. 100°, *Ph* 6-bromo-3:4-methylenedioxybenzyl diketone, m.p. 151°, and α -hydroxy- α -phenyl- β -6-bromo-3:4-methylenedioxyphenylpropionic acid, m.p. 154°. 6-Bromopiperonal and 1:2-OMe-C₆H₄-COMe with NaOH in aq. EtOH afford 1-methoxy-2-naphthyl 6-bromo-3:4-methylenedioxybenzyl ketone, m.p. 147°, and thence the oxide, m.p. 158° (hydrazone, m.p. 185°), 1-methoxy-2-naphthyl α -hydroxy- β -ethoxy-, m.p. 181—182°, and β -formoxy- β -6-bromo-3:4-methylenedioxyphenylethyl ketone, m.p. 158—159°, and 1-methoxy-2-naphthyl 6-bromo-3:4-methylenedioxybenzyl diketone, m.p. 164—165° (quinoxaline derivative, m.p. 203°); the glycolic acid could not be satisfactorily obtained. R. S. C.

Condensation of succinic anhydride with phenols. J. D. RAVAL, K. V. BOKII, and K. S. NARGUND (J. Univ. Bombay, 1938, 7, 184—188).—In (CHCl₃)₂ at 120—135° (CH₂CO)₂O and PhOH give 30—35% of β -o-, m.p. 146° (*Et* ester, b.p. 255°/184 mm.); *Me* ether, m.p. 97—98°, also obtained from o-OMe-C₆H₄-COCl and CO₂Et-CHAc-CH₂-CO₂Et, and 2—3% of β -p-hydroxybenzoylpropionic [γ -keto- γ -p-hydroxyphenylbutyric] acid, m.p. 156° (*Et* ester, m.p. 111°). o-Cresol gives 35—40% of γ -keto- γ -2-, m.p. 136—137° (*Me*, m.p. 78°, and *Et* ester, m.p. 78°; no *Me* ether; blue FeCl₃ colour), and 15—20% of γ -keto- γ -6-hydroxy-m-tolylbutyric acid, m.p. 184° (*Me*, m.p. 108°, and *Et* ester, m.p. 106°). m-Cresol gives 60—65% of γ -keto- γ -3-hydroxy-p-, m.p. 154°, and 1—2% of γ -keto- γ -5-hydroxy-o-tolylbutyric acid, m.p. 172° (also obtained by demethylation of the known *Me* ether). p-Cresol gives 40—45% of 4:1:3-OH-C₆H₃Me-CO-CH₂-CO₂H. R. S. C.

Q (A., II.)

Condensation of maleic anhydride with phenol ethers. K. P. DAVE and K. S. NARGUND (J. Univ. Bombay, 1938, 7, 191—195).—(CH₂CO)₂O and AlCl₃ with PhOMe, o-, m-, and p-C₆H₄Me-OMe, 1:2- and 1:4-C₆H₄(OMe)₂ in the solvent named in parentheses at $\geq 40^\circ$ give β -p-anisoyl- (54% in CS₂), m.p. 129° (*Me*, m.p. 64°, and *Et* ester, m.p. 47°) (cf. Rice, A., 1924, i, 287), β -6-methoxy-m-toluy- (100% in PhNO₂), m.p. 163° (*Me*, m.p. 106°, and *Et* ester, m.p. 60°; dibromide, m.p. 122°), β -5-methoxy-o-toluy- (92% in PhNO₂), m.p. 141° (*Et*, b.p. 209°/11 mm., and *Me* ester, an oil; dibromide, an oil), β -4-methoxy-m-toluy- (82% in PhNO₂, 70% in CS₂), m.p. 126° (*Et* ester, b.p. 197°/17 mm.; dibromide, m.p. 141°), β -4-veratroy- (50% in PhNO₂, 46% in CS₂), m.p. 178° (*Me*, m.p. 91°, and *Et* ester, b.p. 115°/22 mm.; dibromide, m.p. 203°), and β -2:5-dimethoxybenzoyl-, cryst. (*Me*, b.p. 216°/42 mm., and *Et* ester, b.p. 175°/22 mm.; dibromide, m.p. 45°), -acrylic [γ -keto- γ -aryl- Δ^2 -butenoic] acid, respectively. Structures are proved by oxidation by KMnO₄ to ArCO₂H. R. S. C.

Hoesch condensation with ethylene dicyanide [succinonitrile]. G. A. DALAL and K. S. NARGUND (J. Univ. Bombay, 1938, 7, 189—190).—m-C₆H₄(OH)₂, (CH₂CN)₂, ZnCl₂, and HCl in Et₂O give γ -keto- γ -2:4-dihydroxyphenylbutyric acid, m.p. 205° (lit. 199—200°) (*Me*, m.p. 138°, and *Et* ester, m.p. 100°), which with Me₂SO₄ gives the 4-Me (also obtained from m-OH-C₆H₄-OMe) and 2:4-Me₂ ethers. Other phenols do not react. R. S. C.

γ -Ketonic acids. I. P. C. MITTER and S. DE (J. Indian Chem. Soc., 1939, 16, 35—42).—PhOMe, (CH₂CO)₂O, and AlCl₃ in (CHCl₃)₂ at $< 40^\circ$ give β -p-methoxybenzoylpropionic acid, now m.p. 146° (semicarbazone, m.p. 185—186°), reduced (Clemmensen) to γ -p-anisylbutyric acid, new m.p. 61°, which with P₂O₅-C₆H₆ at 100° (bath) affords 1-keto-7-methoxy-1:2:3:4-tetrahydronaphthalene (I), new m.p. 62° (semicarbazone, m.p. 221°). The latter and Zn-Hg in HCl give 7-methoxy-1:2:3:4-tetrahydronaphthalene. (I) and MgMeI give 7-methoxy-1-methyl-3:4-dihydronaphthalene (II), b.p. 124°/5.5 mm., dehydrogenated by So at 310—330° to 1:7-C₁₀H₆Me-OMe, now m.p. 46° (picrate, m.p. 117°). Hydrogenation (PtO₂-EtOH) of (II) gives 7-methoxy-1-methyl-1:2:3:4-tetrahydronaphthalene, b.p. 116°/8 mm. 1:2:3-C₆H₃(OMe)₃ (as above in place of PhOMe) affords β -2-hydroxy-3:4-dimethoxybenzoylpropionic acid, m.p. 152°, thence γ -2-hydroxy-3:4-dimethoxyphenylbutyric acid, m.p. 103°, converted by 85% H₂SO₄ at 100° (bath) into 5-hydroxy-1-keto-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene, m.p. 155° (semicarbazone, m.p. 226°), which with Zn-Hg in HCl gives 5-hydroxy-6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene, b.p. 148—154°/5.5 mm. m-C₆H₄(OMe)₂ (as above) affords a mixture of keto-acids, converted by H₂SO₄-EtOH into β -2-hydroxy-4-methoxybenzoylpropionic acid, m.p. 154° (semicarbazone, m.p. 198°), and *Et* β -2:4-dimethoxybenzoylpropionate, m.p. 66°, b.p. 198—200°/5 mm. The latter is hydrolysed (10% KOH) to the acid, m.p. 147° (semicarbazone, m.p. 166°), converted by Zn-Hg in HCl into γ -2:4-dimethoxyphenylbutyric acid, m.p. 49°, b.p. 199—201°/5 mm., which could not be cyclised (inhibition effects dis-

cussed). PhOH (as above) at 130–140° gives β -o-hydroxybenzoylpropionic acid, m.p. 145°, reduced to γ -o-hydroxyphenylbutyric acid, m.p. 67°, which could not be cyclised. Attempted prep. of acenaphthene derivatives by condensing (I) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}\cdot\text{Zn}$, and subsequent ring-closure was impracticable owing to the poor yield of the Reformatsky condensation.

A. T. P.

Fission of ketones by alkalis. III. Benzophenones. G. LOCK and E. RÖDIGER (Ber., 1939, 72, [B], 861–870; cf. A., 1939, II, 215).—Fission of COPh_2 is more difficult than that of COPhMe so that 50% KOH at 150° requires to be replaced by a molten mixture of 40 mol.-% KOH and 60 mol.-% NaOH. At 200° or 250°, COPh_2 gives C_6H_6 and ~86% of BzOH; further increase of temp. does not increase the yield of acid owing to the simultaneous production of ~5% of $\text{CPh}_3\cdot\text{OH}$. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COPh}$ is less reactive than COPh_2 but at 250° it gives C_6H_6 , PhMe, BzOH, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$. Similarly *o*- and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COPh}$ afford C_6H_6 , PhMe, and a mixture of BzOH and *o*- (~17%) or *m*- (~50%) $\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$, respectively. *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COPh}$ and other Cl-derivatives are more readily decomposed than the homologues; it gives solely PhCl and BzOH. *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COPh}$ also gives PhCl with a mixture of ~80% of BzOH and 5% of *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COPh}$ yields about 18% of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ and 66% of BzOH with a small quantity of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ and about 8% of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. 2:4-, 2:5-, 2:6-, and 3:5-Di- and 2:3:4:5:6-penta-chlorobenzophenone are smoothly converted into BzOH and the di- or penta-chlorobenzene. *o*- and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ are acted on under the same conditions as the chlorobenzophenones whereby much resinous product is formed in addition to BzOH. *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ gives some $(\text{NPh})_2$ apparently formed by the action of alkali on PhNO_2 produced during the change.

2:4-Dichlorobenzhydrol, b.p. 202–205° (corr.)/14 mm. (from 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CHO}$ and MgPhBr), 2:6-dichlorobenzophenone, m.p. 86°, 3:5-dichlorobenzylidene bromide, m.p. 64°, and 3:5-dichlorobenzhydrol, b.p. 217–218°/20 mm., appear to be new.

H. W.

Biochemistry of micro-organisms. LXI. Molecular constitution of geodin and erdin, two chlorine-containing metabolic products of *Aspergillus terreus*, Thom. II. Dihydro-geodin and -erdin. Synthesis of their trimethyl ethers. C. T. CALAM, P. W. CLUTTERBUCK, A. E. OXFORD, and H. RAISTRICK (Biochem. J., 1939, 33, 579–588; cf. A., 1936, 1116; 1937, II, 385).—Dihydroerdin (I) is shown to be 3:5-dichloro-2:6:6'-trihydroxy-4'- or -2:6:4'-trihydroxy-6'-methoxy-4-methylbenzophenone-2'-carboxylic acid. Dihydrogeodin (II) is its Me ester. Towards phenolphthalein they titrate as di- and mono-basic acid, respectively. With $\text{CHMeN}_2\cdot\text{Et}_2\text{O}$, followed by $\text{NaOH}\cdot\text{aq. EtOH}$, (I) and (II) give dihydroerdin Et_3 ether, m.p. 211–213°. Dihydroerdin Me_3 ether (III) and $\text{Ac}_2\text{O}\cdot\text{AcOH}\cdot\text{NaOAc}$ at 150–160° give a neutral Ac derivative, m.p. 208–210°, the γ -keto-acid reacting as a γ -hydroxy- γ -lactone (proof of the *o*-relation of the CO and CO_2H). KMnO_4 oxidises (III) in aq. NaOH to an acid, $\text{C}_{19}\text{H}_{16}\text{O}_9\text{Cl}_2$, m.p. 233–235°, hydrolysed by

80% H_2SO_4 at 110° to 3:5-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ (IV) and 2:6:3:5:1:4-(OMe) $_2\text{C}_6\text{Cl}_2(\text{CO}_2\text{H})_2$. No product could be isolated after KMnO_4 oxidation of partly methylated (I). HI (*d* 1.7) converted (II) in N_2 at 140–150° into MeI (2 mols.), CO_2 (1 mol.), orcinol, and 3:5-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$; the same products (but 1 mol. of MeI are obtained from (I). 80% H_2SO_4 at 120° hydrolyses (I) or (II) to 3:5:1-OH $\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CO}_2\text{H}$ and 2:6-dichloro-3:5-dihydroxy-*p*-toluic acid (V), m.p. 214° [above 214° yields 2:6-dichloro-orcinol (VI), m.p. 164°]; (III) gives similarly (IV), CO_2 , 3:1:2:6:5:4-OH $\cdot\text{C}_6\text{MeCl}_2(\text{OMe})\cdot\text{CO}_2\text{H}$, and 1:2:6:3:5- $\text{C}_6\text{HMeCl}_2(\text{OMe})_2$ (VII). When heated at 250°, erdin, geodin, or (I) gives (VI), converted by CH_2N_2 into (VII). 3:5:1:2:6:4-(OMe) $_2\text{C}_6\text{MeCl}_2\cdot\text{COCl}$ (VIII) (prep. from the acid by SOCl_2), 3:5-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{Me}$, and AlCl_3 give a product, converted by $\text{Me}_2\text{SO}\cdot\text{aq. NaOH}$, followed by $\text{NaOH}\cdot\text{EtOH}$, into (III), m.p. 177–179° (lit. 168°), and thence by CH_2N_2 into dihydrogeodin Me_3 ether, m.p. 110–112°. *m*- $\text{C}_6\text{H}_4(\text{OMe})_2$ with (VIII) and AlCl_3 etc. gives 3:5-dichloro-2:6:2':4'-tetramethoxy-4-methylbenzophenone, m.p. 94–95°, which, however, could not be prepared by decarboxylation of (III). 1:3:5- $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2$ gives similarly 3:5-dichloro-2:6:2':4'-tetramethoxy-4:6'-dimethylbenzophenone, m.p. 105–106° (could not be oxidised to a dicarboxylic acid), and some (V).

R. S. C.

Reactions catalysed by aluminium chloride. XVIII. Condensation of 9:10-dihydroanthracene with acid chlorides. C. D. NENITZESCU, I. GAVĂT, and D. COCORĂ (Ber., 1939, 72, [B], 819–820).—Freshly sublimed AlCl_3 , BzCl, and 9:10-dihydroanthracene in CS_2 at room temp. give 9-benzoyl-9:10-dihydroanthracene, m.p. 104°, oxidised (CrO_3 in AcOH at 100°) to anthraquinone and dehydrogenated (S at 180°) to 9-benzoylanthracene, m.p. 148°. Similarly, AcCl yields 9-acetyl-9:10-dihydroanthracene, b.p. 150–151°/3 mm. (oxime, m.p. 148–149°), converted by Pd-C at 320° into anthracene.

H. W.

Anionotropic and prototropic changes in cyclic systems. VI. *cis*- and *trans*-3:4-Diphenylcyclopentanones. Structure of the ketone obtained by reduction of 2-hydroxy-3:4-diphenyl- Δ^2 -cyclopentenone with hydriodic acid. H. BURTON and C. W. SHOPPEE (J.C.S., 1939, 567–573; cf. A., 1934, 409).—2-Hydroxy-3:4-diphenyl- Δ^2 -cyclopentenone (von Liebig, A., 1914, i, 845) is reduced ($\text{Na}\cdot\text{Hg}$) to 3:4-diphenylcyclopentane-1:2-diol, m.p. 114°, and *cis*- (I) (oxime, m.p. 137–138°; 2:4-dinitrophenylhydrazones, m.p. 208°; dipiperonylidene derivative, m.p. 240°), and *trans*-3:4-diphenylcyclopentanone (II) (oxime (+ $x\text{MeOH}$), m.p. 109–113°, “anhyd.” 121.5°; 2:4-dinitrophenylhydrazones, m.p. 170°; dipiperonylidene derivative, m.p. 220°) (cf. Weidlich, A., 1938, II, 400). 3:4-Diphenyl- Δ^3 -cyclopentenone [2:4-dinitrophenylhydrazones, m.p. 259–260° (decomp.); cf. Allen et al., A., 1937, II, 457] is reduced (H_2 , Pt-black, EtOH) to (I), by $\text{H}_2\cdot\text{PtO}_2\cdot\text{EtOH}$ to *cis*-3:4-diphenylcyclopentanol, m.p. 85–86° [oxidised (CrO_3) to (I)], and by $\text{Na}\cdot\text{EtOH}$ to a mixture of alcohols, oxidised (CrO_3) to (I) and

(II). Reduction (Zn-Hg + HCl) of (I) and (II) yields *cis*- and *trans*-1 : 2-diphenylcyclopentane (III), respectively. The "3 : 4-diphenylcyclopentanone" obtained (Allen *et al.*, *loc. cit.*) by reducing 2-hydroxy-3 : 4-diphenyl- Δ^2 -cyclopentenone with HI and P is really a 2 : 3-diphenylcyclopentenone (IV) (oxime, decomp. 257—258° after previous darkening and sintering). It is reduced by Zn-Hg + HCl to (III), and by H_2 -PtO₂ to *trans*-2 : 3-diphenylcyclopentanone (V), m.p. 98° [oxime, m.p. 187°; semicarbazone, m.p. 195—196° (decomp.)]; 2 : 4-dinitrophenylhydrazones, m.p. 142°, which is also reduced (Zn-Hg + HCl) to (III), and with piperonal and NaOEt or MeOH-KOH yields a substance, C₂₅H₂₂O₄, m.p. 190°; (V) is also accompanied by varying amounts of the cyclopentanol, b.p. 160°/0.5 mm. [oxidised (CrO₃) to (V)]. Oxidation of (IV) in acid solution yields only BzOH; KOBz in aq. dioxan yields diphenylmaleic anhydride and (?) CO₂H·[CHPh]₂·CH₂·CO₂H, but no BzOH. (I) with BrinCHCl₃ yields 2-bromo-*cis*-3 : 4-diphenylcyclopentanone, m.p. 91° (turbid; clear at 98°), which with C₅H₅N at 35° or the b.p. gives only 3 : 4-diphenyl- Δ^3 -cyclopentenone [similarly obtained from (II)]. This with O₃ can react as the Δ^2 -ketone, giving some C₆H₅·CHPh·CH₂·CO₂H. 5-Chloro-*trans*-2 : 3-diphenylcyclopentanone, m.p. 137° [from (V) and Cl₂ at 102°], yields amorphous products with boiling C₅H₅N.

A. Li.

Catalytic oxidation of cyclohexylamine. V. S. SMIRNOV (J. Gen. Chem. Russ., 1938, 8, 1727—1729).—Aq. cyclohexylamine and O₂ in presence of Cu at room temp. yield cyclohexanone.

R. T.

Kinetics of oxidation of ketones with selenium dioxide.—See A., 1939, I, 327.

Action of organo-magnesium compounds on 1-chlorocyclohexyl methyl and phenyl ketone; secondary replacement of chlorine by a pinacolic change. O. SACKUR (Compt. rend., 1939, 208, 1092—1094; cf. A., 1934, 654; 1939, II, 67).—1-Chlorocyclohexyl Ph ketone with MgMeI or 1-chlorocyclohexyl Me ketone (I) with MgPhBr in Et₂O first at -10°, then at the b.p., and finally at 130° (no solvent) affords 1-phenylcyclohexyl Me ketone (II), m.p. 35° (semicarbazone, m.p. 223—224°; oxime, m.p. 137—138°), which indicates the migration of Ph in the intermediate C₆H₁₀Cl·CPhMe·OH. Similarly (I) or 1-methylcyclohexylcarboxylamide with MgMeI affords 1-methylcyclohexyl Me ketone, b.p. 80—85°/16 mm. (semicarbazone, m.p. 182°). α -Methylbenzylidenecyclohexane with BzO₂H affords the corresponding epoxide, b.p. 157—158°/16 mm., which when heated at 300° on infusorial earth, or with ZnCl₂, or with MgBr₂ etherate affords 2-phenyl-2-methylcycloheptanone (?), which indicates that (II) is not formed from the Ph ketone via the epoxide.

J. L. D.

spiro-Compounds. V. Formation and transformation of spiro-compounds from 3- and 2-methylcyclohexanones. N. N. CHATTERJEE and G. N. BARPUJARI (J. Indian Chem. Soc., 1938, 15, 639—645; cf. A., 1937, II, 19, 62, 377, 418).—1-Hydroxy-1-cyano-3-methylcyclohexane, b.p. 132—135°/20 mm., with CN·CHNa·CO₂Et in EtOH, followed by CH₂Cl·CH₂·CO₂Et, gives Et₂ α -cyano- α -

(1-cyano-3-methylcyclohexyl)glutarate (I), b.p. 216°/5 mm., hydrolysed to α -(1-carboxy-3-methylcyclohexyl)glutaric acid (II), m.p. 185° (decomp.), the anhydride of which in EtOH-H₂SO₄ with EtOH vapour gives α -(1-carbethoxy-3-methylcyclohexyl)glutaric anhydride, b.p. 187°/4 mm. The Et₃ ester, b.p. 184°/5 mm., of (II) (esterified as above) with Na in C₆H₆ forms Et₂ 3-methylcyclohexanespirocyclopentan-2'-one-3' : 5'-dicarboxylate, b.p. 185—190°/5 mm. This is hydrolysed (20% H₂SO₄) to 3-methylcyclohexanespirocyclopentan-2'-one-5'-carboxylic acid (III), m.p. 140—143° [Et ester, b.p. 135—140°/4 mm. (semicarbazone, m.p. 185° after previous softening)], also obtained from the Na salt of (II) and Ac₂O at 130—140°, followed by EtOH-H₂SO₄, and hydrolysis by aq. EtOH-NaOH. Zn-Hg-HCl reduction of (III) yields 3-methylcyclohexanespirocyclopentan-5'-carboxylic acid, m.p. 62—65° (previous softening), converted by Se at 280—290° into 2-C₁₀H₇·Me. Et₂ α -cyano- α -(1-cyano-2-methylcyclohexyl)glutarate, m.p. 61°, b.p. 212°/5 mm., obtained similarly to (I), is hydrolysed to α -(1-carboxy-2-methylcyclohexyl)glutaric acid, m.p. 170° (decomp.) (anhydride Et ester, b.p. 185—190°/4 mm.), the Et₃ ester, b.p. 187°/4 mm., of which gives Et₂ 2-methylcyclohexanespirocyclopentan-2'-one-3' : 5'-dicarboxylate, b.p. 180—185°/4 mm., and -5'-carboxylate, b.p. 142—148°/6 mm. (semicarbazone, m.p. 202°).

E. W. W.

Oximes of 4 : 4'-dinitrobenzil. W. BRYDOWNA (Rocz. Chem., 1938, 18, 396—403).—

(p-NO₂·C₆H₄·CO)₂ (I) heated with NH₂OH·HCl and NaOAc in MeOH yields α -4 : 4'-dinitrobenzilmonoxime (II), m.p. 193—194° (decomp.) (Cu^{II}, Co^{II}, Fe^{II} salts), the Ac derivative, m.p. 139—140°, of which with 1% NaOH yields p-NO₂·C₆H₄·CN (III) and p-NO₂·C₆H₄·CO₂H (IV). A mixture of the α - and β -monoxime (V), m.p. 164—166° (Ac derivative, m.p. 157—158°), is obtained from (I) and NH₂OH·HCl in boiling EtOH. (V) is instantaneously converted by 1% NaOH into (III) and (IV), and by heating at 165° into (II). By the Beckmann rearrangement (V) yields p-nitrobenzoylform-p-nitroanilide, p-NO₂·C₆H₄·CO·CO·NH·C₆H₄·NO₂-p, m.p. 142—147° (dioxime, m.p. 251—253°), readily decomp. to yield (IV) and p-NO₂·C₆H₄·NH₂. (II) with PCl₅ in Et₂O gives (III), (IV), and (p-NO₂·C₆H₄·CO)₂NH. (I) and excess of NH₂OH·HCl with NaOAc in boiling EtOH (20 hr.) afford the α -dioxime, m.p. 268—270° (decomp.) (Ni^{II}, Co^{II}, Fe^{II} salts); the β -dioxime, m.p. 245—246°, obtained similarly in absence of NaOAc, gives (p-NO₂·C₆H₄·NH·CO)₂ by the Beckmann rearrangement.

R. T.

Action of selenium dioxide on pulegone. G. CAUQUIL (Compt. rend., 1939, 208, 1156—1158; cf. A., 1936, 471).—Pulegone (I) with SeO₂ in EtOH or cyclohexane at 80° affords unchanged (I), 3-methyl-6-isopropylidenecyclohexane-1 : 2-dione (II), b.p. 154°/17 mm. (semicarbazone, m.p. 269°) [oxidised (H₂O₂) to α -methylglutaric acid], 3-methyl-6-isopropylidenecyclohexane-1 : 2 : 5-trione (III), m.p. 186° [also obtained from (II) with SeO₂], and (in EtOH) 2-ethoxy-3-methyl-6-isopropylidene- Δ^3 or Δ^4 -cyclohexenone, b.p. 140°/17 mm., and 5-ethoxy-3-methyl-6-isopropylidene- Δ^3 or Δ^4 -cyclohexene-1 : 2-dione, b.p. 161—162°/17

mm. (semicarbazone, m.p. 252°). (III) is oxidised (HNO₃) to α -keto- β -methylglutaric and other acids.

J. L. D.

Isomerisation of 2:2-disubstituted indanediones. G. N. GHEORGHIU (Bull. Soc. chim., 1939, [v], 6, 493—501; cf. A., 1934, 527; 1936, 1508).—With EtOH—NaOEt in H₂, Et 2-methylindano-1:3-dione-2-acetate gives Et 1:4-dihydroxy-3-methyl-2-naphthoate, m.p. 96—97° [diacetate (I), m.p. 126—127°], slowly oxidised by air in EtOH to the 1:4-quinone (II), m.p. 100—101° [reductive acetylation affords (I)]. Oxidation in aq. EtOH—alkali gives (II) and 3-hydroxy-2-methyl-1:4-naphthaquinone (III), m.p. 172—173° (acetate, m.p. 107—108°; 1-mono-phenylhydrazone, m.p. 182—183°), reduced and acetylated to 1:3:4-triacetoxy-2-methylnaphthalene, m.p. 146—148°. The corresponding Me ester isomerises to Me 1:4-dihydroxy-3-methyl-2-naphthoate, m.p. 94—96°, oxidised in alkaline solution to (III), and in EtOH to the 1:4-quinone, m.p. 96—97°. 2-Phenyl-2-acetonilindane-1:3-dione yields 1:4-dihydroxy-3-acetyl-2-phenylnaphthalene, m.p. 131—132° (diacetate, m.p. 165—166°; Me₂ ether, m.p. 160—162°). 2-Phenyl-2-benzylindane-1:3-dione with NaOEt yields *o*- α - β -diphenylpropionylbenzoic acid, m.p. 166—167° (Ag salt).

A. Li.

Syntheses in the sterol and sex hormone group.
II. Synthesis of a 3-ketohexahydrochrysene. C. K. CHUANG, Y. T. HUANG, and C. M. MA (Ber., 1939, 72, [B], 713—716; cf. A., 1937, II, 294).—Gradual addition of γ -1-naphthylbutyryl chloride (in C₆H₆) to Et₂ α -acetylglutarate and Na powder (in C₆H₆) gives Et δ -keto- γ -carbethoxy- γ -acetyl- η -1-naphthylctoate, hydrolysed to (impure) δ -keto- η -1-naphthylctoic acid, which is treated with CH₂N₂ and then cyclised by NaOEt in Et₂O to 2:6-diketo-1- β -1'-naphthylethylcyclohexane, m.p. 199—200°. This is transformed by P₂O₅ in C₆H₆ into 3-ketohexahydrochrysene, m.p. 160—161° (oxime, m.p. 235—236° in a bath preheated to 225°), reduced (Clemmensen) and then dehydrogenated (Se at 310—320°) to chrysene.

H. W.

Sulphonation of cholestenone as 1:4-addition. E. KUHR (Ber., 1939, 72, [B], 929—930).—Sulphonation of cholestenone enol acetate leads in equally good yield to Δ^4 -cholestenone-6-sulphonic acid (I) (A., 1937, II, 504). SO₃H is added at C₆, and OH at C₃, whilst AcOH is immediately eliminated. Similarly 3-chloro- $\Delta^{3:5}$ -cholestadiene instantaneously gives HCl and (I), the change being explicable only by the hypothesis of 1:4-addition. The similar course of the change shows that cholestenone is sulphonated in its enol form. In the case of cholesterolene the change is more difficult and is accompanied by oxidations. Probably substitution occurs directly at C₆.

H. W.

Sterols. LIV. Pregnan-20-one, allopregnan-20-one, and their reduction products. R. E. MARKER and E. J. LAWSON (J. Amer. Chem. Soc., 1939, 61, 852—855; cf. A., 1939, II, 261).—Crude pregnan-20(α)-ol-3-one acetate semicarbazone, m.p. 200—204° (decomp.), and NaOEt—EtOH at 180° give only (85%) pregnane-3(α):20(α)-diol. Zn—Hg and HCl in AcOH reduce pregnan-20(α)-ol-3-one

acetate mainly to hydrocarbons, but in EtOH [and subsequent hydrolysis (EtOH—NaOH)] a good yield of pregnan-20(α)-ol (I), m.p. 146° (acetate, m.p. 130°), is obtained. CrO₃—AcOH oxidises (I) to pregnan-20-one (II), m.p. 116° [semicarbazone, m.p. 237° (decomp.); 2:4-dinitrophenylhydrazone, m.p. 240° (decomp.)]; also obtained from pregnanediolone by HCl—Zn—EtOH, but even an excess of CrO₃ at 100° gives only traces of acid. H₂—PtO₂ at 40 lb. reduces (II) in AcOH to pregnan-20(β)-ol, cryst. (acetate, m.p. 85°), and 20% of a mixture of hydrocarbons (? including pregnane). Zn—HCl—EtOH reduction of allopregnan-20(α)-ol-3-one gives allopregnan-20(α)-ol (III), m.p. 136° (acetate, m.p. 94°), and a carbinol, C₂₁H₃₆O₄, m.p. 229° (diacetate, m.p. 162°); allopregnanediolone similarly gives allopregnan-20-one, m.p. 129° [semicarbazone, m.p. 260° (decomp.)]; 2:4-dinitrophenylhydrazone, m.p. 220—223°, also obtained from (III) by CrO₃ and hydrogenated (PtO₂, AcOH) to allopregnan-20(β)-ol, m.p. 140° (acetate, m.p. 156°), also obtained by reduction (Zn—EtOH—HCl) of allopregnan-20(β)-ol-3-one acetate.

R. S. C.

Preparation of constituents of the adrenal cortex and related substances. β - Δ^4 -Pregnene-17:20:21-triol-3-one. W. LOGEMANN (Naturwiss., 1939, 27, 196—197; cf. A., 1938, II, 322).— Δ^4 :17-Pregnen-21-ol-3-one (I) and OsO₄ give β - Δ^4 -pregnene-17:20:21-triol-3-one (II), m.p. 189—190°, [α]_D²⁰ +63° in dioxan (diacetate, m.p. 189—190°, [α]_D²⁰ +125° in dioxan), which has the configuration at C₁₇ of the natural substances of the cortex. (I) and (II) have no cortin or corpus luteum hormone activity.

R. S. C.

Substituted ketocholanic acids. S. BERGSTROM and G. A. D. HASLEWOOD (J.C.S., 1939, 540—541).—11:12-Diketocholelanic acid (Wieland *et al.*, A., 1931, 841) yields a monosemicarbazone, m.p. 240—242° (decomp.) [hydrolysed (MeOH—dil. H₂SO₄, followed by NaOEt) to 11-hydroxy-12-keto- Δ^9 :11-cholelanic acid (*loc. cit.*)], which with EtOH—NaOEt at 165—175° under pressure yields a triazine, C₂₅H₄₁O₃N₃, m.p. 292—295° (decomp.) [Me ether Me ester (CH₂N₂), m.p. 142—143°]. The semicarbazones of 3-hydroxy-12-keto- and -7:12-diketo-cholelanic acid (from cholic acid by direct oxidation with CrO₃; cf. Kaziro *et al.*, A., 1937, II, 500) with EtOH—NaOEt both yield lithocholic acid (Me ester acetate, m.p. 128—130°), which is thus readily obtainable.

A. Li.

Preparation of progesterone from cholesterol. M. A. SPIELMAN and R. K. MEYER (J. Amer. Chem. Soc., 1939, 61, 893—895).—Crude progesterone (I) is most conveniently prepared from cholesterol (1.8 rabbit units from 1 g.) by brominating in C₆H₆, oxidising with KMnO₄, and debrominating. Complete purification is difficult. Cholestenone (50%) is also obtained; this yields 2 units of (I) per g. by the method of Dirscherl *et al.* (A., 1938, II, 147), but none by that of Tavastjerna (Arch. Sci. biol. U.S.S.R., 1936, 40, 141).

R. S. C.

Absolute values of the velocity constants in the formation of semiquinone.—See A., 1939, I, 327.

1:4-Tetra-azidobenzquinone. F. ŠORM (Chem. Obzor, 1939, 14, 37—39).—Finely powdered O:C₆Cl₄:O and NaN₃ in EtOH suspension give 1:4-

tetra-azidobenzoquinone (I), blue-black, reduced to tetra-azidoquinol, colourless, which ignites in a flame, whereas (I) explodes violently. (I) is of no use as an explosion initiator owing to its instability.

F. R.

Homonuclear 2-hydroxy-1-methylanthraquinones. C. MARSHALK (Bull. Soc. chim., 1939, [v], 6, 655—664).—2-Hydroxyanthraquinone and aq. $\text{Na}_2\text{S}_2\text{O}_4$ - Na_2CO_3 in N_2 with CH_2O at 90—95° for 1 hr. give 2-hydroxy-1-methylanthraquinone (I), m.p. 240° (Ac derivative, m.p. 186°) (cf. Waldmann *et al.*, A., 1938, II, 194). Its Me ether (II), m.p. 214—215°, is oxidised (MnO_2 - H_2SO_4 at respectively 5° and at <15°) to 1-aldehydo-2-methoxyanthraquinone, m.p. 242° (247—248° on block), and 2-methoxyanthraquinone-1-carboxylic acid, m.p. 275—276° (block) (decomp.), also obtained by methylating the 2-OH-acid, new m.p. 265° (decomp.). (I) and HNO_3 - H_2SO_4 - H_3BO_3 at 0—5°, then at room temp., give 3-nitro-2-hydroxy-1-methylanthraquinone (III), m.p. 222—223°, reduced by aq. $\text{Na}_2\text{S}_2\text{O}_4$ - Na_2CO_3 to the 3- NH_2 -derivative, m.p. 264° (block). (II) and H_2SO_4 - HNO_3 at 5—10°, then at room temp., or (III) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ in PhNO_2 - Na_2CO_3 give 3-nitro-2-methoxy-1-methylanthraquinone, m.p. 157—158°, reduced by excess of aq. Na_2S to the 3- NH_2 -derivative, m.p. 223—224°.

A. T. P.

Natural hydroxy- and hydroxy-methyl-anthraquinones and synthesis of anthraquinone derivatives. R. EDER and B. STEGFRIED (Pharm. Acta Helv., 1939, 14, 34—76).—A complete survey is given of the natural hydroxyanthraquinones, together with general properties and bibliography. The regularity of the structure of vegetable anthraquinone derivatives is discussed. 3:1:2- NO_2 - $\text{C}_6\text{H}_3(\text{CO})_2\text{O}$ (I), *p*-cresol, and AlCl_3 at $\geq 130^\circ$ for 3 hr. give 3-nitro-2-(4-hydroxy-*m*-toluoyl)benzoic acid (II), m.p. 256.5—257.5°. Use of H_3BO_3 in place of AlCl_3 at 170—180° gives (II), less of the isomeric 6- NO_2 -acid (III), m.p. 215.2—216.2°, and a little 6'(or 3')-nitro-2:7-dimethylfluoran, m.p. 249.5°. (II) and (III) are reduced by $\text{Fe}(\text{OH})_2$ -aq. NH_3 to the corresponding NH_2 -acids, m.p. 235—236° (decomp.) and 207.5—208° (decomp.), respectively, and thence by the diazo-reaction to 3- (IV), m.p. 194.5—195.5°, and 6-hydroxy-2-(4-hydroxy-*m*-toluoyl)benzoic acid (V), m.p. 184.5—185.5°, respectively. (IV) and (V) with H_2SO_4 , H_2O and H_3BO_3 followed by 25% oleum at 70° (90°) give 1:8-, m.p. 211—212° (diacetate, m.p. 201—202°), and 1:5-dihydroxy-4-methylanthraquinone, m.p. 234—234.5° (diacetate, m.p. 227—228°), respectively. (III) and H_2SO_4 , H_2O - H_3BO_3 at 95° give 5-nitro-1-hydroxy-4-methylanthraquinone, m.p. 236.5—237° (decomp.) [acetate, m.p. 239—239.5° (decomp.)]. (I) and *o*-cresol- H_3BO_3 at 170—180° give 3-, m.p. 236.5—237.5°, and 6-nitro-2-(2-hydroxy-*m*-toluoyl)benzoic acid, m.p. 222.5—223.5°; the former gives the 3- NH_2 -, m.p. 241—242° (decomp.), and thence the 3-OH-acid (VI), m.p. 175—176° (sinters. $\sim 168^\circ$) (together with a compound, $\text{C}_{15}\text{H}_{10}\text{O}_2$, m.p. 246—247°). Ring closure of (VI) gives 1:8-dihydroxy-2-methylanthraquinone, m.p. 176.5—177° (diacetate, m.p. 203—204°). The "sen-nachrysophanic acid" of Tschirch and Hiepe (A., 1900, i, 681) is impure chrysophanol. Extinction

curves for 1:5- and 1:8-dihydroxyanthraquinone and their 4-Me derivatives are given. M.p. are corr.

A. T. P.

Metabolic products of *Penicillium funiculosum*, Thom. I. Red pigment, funiculosin. H. IGARACI (J. Agric. Chem. Soc. Japan, 1939, 15, 225—228).—Funiculosin, $\text{C}_{15}\text{H}_{10}\text{O}_5$, m.p. 218° (tri-acetate, m.p. 205°; tribenzoate, m.p. 277°), has been isolated from *P. funiculosum* grown in a decoction of koji. Distillation with Zn yields anthracene. Funiculosin is probably a trihydroxymethylanthraquinone or dihydroxyhydroxymethylanthraquinone.

J. N. A.

Bromination of anthraquinone-2-sulphamic acid. W. LEŚNIAŃSKI and H. W. TURSKA-JAROSZEWICZOWA (Rocz. Chem., 1938, 18, 680—687).—Aq. Br is added in 10% excess to aq. Na anthraquinone-2-sulphamate at p_H 6.5 (room temp.). Aq. Na_2CO_3 is added at intervals, to maintain the p_H at 6.5, until free Br is no longer present, when the solution is made feebly alkaline, boiled, and then made strongly acid. The yield of 1-bromo-2-aminoanthraquinone is 83% on the aminoanthraquinone originally taken.

R. T.

β -Phellandrene.—See B., 1939, 550.

Total synthesis of pinene. G. KOMPPA, A. KLAM, and A. M. KUVAJA (Naturwiss., 1939, 27, 197—198).—*l*-Verbenone and NaNH_2 - CO_2 give verbanonecarboxylic acid, reduced electrolytically to the OH-acid, which is dehydrated by Ac_2O to d-8-pinene-carboxylic acid. This gives 1-pinocamphone, b.p. 212—214° (semicarbazone, m.p. 226—228°), by way of the acid chloride, azide, carbimide, and amine. No details are given.

R. S. C.

High mol. wt. esters of ortho-acids. V. G. MCHITARIAN (J. Gen. Chem. Russ., 1938, 8, 1361—1368).— $\text{CH}(\text{OEt})_2\cdot\text{OR}$ [$\text{R} = \text{dl-bornyl-}$ (I), b.p. 132—134°/12.5—13 mm.; $\text{R} = \text{dl-menthyl-}$, b.p. 140—142°/13.5 mm.; $\text{R} = \text{l-menthyl-}$, b.p. 135—140°/14 mm., $[\alpha]_D^{20} -77.97^\circ$ in C_6H_6], $\text{CH}(\text{OEt})(\text{OR})_2$ [$\text{R} = \text{dl-bornyl-}$ (II), b.p. 192—194°/9—10 mm.; $\text{R} = \text{dl-menthyl-}$, b.p. 205—206°/13.5 mm.; $\text{R} = \text{l-menthyl-}$, b.p. 195—197°/11 mm., $[\alpha]_D^{20} -116.74^\circ$ in C_6H_6], and $\text{CH}(\text{OR})_3$ [$\text{R} = \text{dl-bornyl-}$ (III), m.p. 231—235°; $\text{R} = \text{dl-menthyl-}$, m.p. 130—131°; $\text{R} = \text{l-menthyl-}$, m.p. 71.5—72°, $[\alpha]_D^{20} -133.69^\circ$ in C_6H_6] are prepared by heating $\text{CH}(\text{OEt})_3$ with menthol or borneol in presence of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$. (II) yields (I) and (III) when exposed to light.

R. T.

Different forms of β -ethylhydroxycampholic acid, and their transformation. J. VÈNE (Bull. Soc. chim., 1939, [v], 6, 683—691; cf. A., 1938, II, 446).— β -Ethyl- β -campholide and NaOEt give β -ethylhydroxycampholic acid, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CHET}\cdot\text{OH}$, m.p. 73°, $[\alpha]_D^{20} +33.3^\circ$ in EtOH. Slow crystallisation from Et₂O-ligroin, CHCl_3 , EtOAc, or C_6H_6 gives a form A, m.p. 73° (two types of crystal); crystallisation from EtOH at 95°, or aq. EtOH, affords a form B, m.p. 87°, $[\alpha]_D^{20} +37.6^\circ$ in EtOH (one cryst. type). A or B on slow heating to 110° gives, with loss in wt. of 8 and 3%, respectively, a form C, m.p. 105°, $[\alpha]_D^{20} +40.5^\circ$ in EtOH, transformed into A or B by crystallising from Et₂O-ligroin or aq. EtOH, respectively. A, finely-ground and left in air saturated with H₂O

vapour at room temp. for 24 hr., gives *B*, reconverted into *A* by Et₂O-ligroin. In *A* → *B* loss in wt. varies with the nature of solvent used for crystallising *A*, and may be due to partial volatilisation and some hydration. *A* and *B* contain some solvent of crystallisation and *B* is partly hydrated. A. T. P.

Action of organomagnesium derivatives on methyl camphoraldehyde. J. VÈNE (Bull. Soc. chim., 1939, [v], 6, 672—697; cf. A., 1938, II, 446).—CHO·C₈H₁₄·CO₂Me (I) (*loc. cit.*) and MgEtBr in Et₂O afford β-ethylcampholide and some (?) β-campholide. Higher temp. give a mixture of (?) CH₂:CMe·C₈H₁₄·CHMe·OH,

CH₂:CMe·C₈H₁₄·CH:CH₂, and C₈H₁₄< $\begin{smallmatrix} \text{CMe}_2 \\ \text{CHMe} \end{smallmatrix}$ >O. In PhMe (110°) and xylene (140°), similar mixtures are obtained, with some (?) OH·CMe₂·C₈H₁₄·CHMe·OH and (?) isomeride of β-ethylcampholide, respectively. A similar result is obtained with (I) and MgMeI·Et₂O-xylene. A. T. P.

Catalytic reduction of camphorquinone in presence of methylamine. 3-Methylamino-2-hydroxycamphane and its pharmacodynamic properties. F. P. MAZZA and C. MIGLIARDI (Ber., 1939, 72, [B], 689—697).—Hydrogenation (PtO₂) of camphorquinone and NH₂Me in abs. EtOH gives a mixture of the stereoisomeric forms of 3-methylamino-2-hydroxycamphanes [3-methylaminoisoborneol (I), a liquid, b.p. 135°/700 mm., and 3-methylamino-borneol (II), m.p. 81—82° in sealed capillary], separated from one another by utilising their differing solubilities in Et₂O and purified through the hydrochlorides, m.p. 247° (corr.) in sealed tube and decomp. ~253°, which have a very sweet and a bitter taste respectively. (I) yields a *platinichloride*, m.p. 197°, *picrate*, m.p. 217° (decomp.) after becoming brown at 195°, *picrolonate*, m.p. 228°, *flavianate*, m.p. 192°, and *reineckate*, m.p. 190°. (II) gives a *platinichloride*, m.p. 209°, *picrate*, m.p. 189°, *picrolonate*, decomp. 215°, *flavianate*, decomp. 199°, and *reineckate*, m.p. 210°. Some photomicrographs are given. (I) and (II) are converted by CH₂N₂ in Et₂O into non-cryst. Me ethers which give *hydrochlorides*, m.p. 212° and — respectively. Oxidation of (I) by Cl₂-H₂O gives 3-methylaminocamphor hydrochloride, also obtained from (II) by oxidation with CrO₃ but not with Cl₂-H₂O. The bases have extraordinary physiological activity. H. W.

Rotatory power and chemical constitution. IV. M. SINGH (J. Indian Chem. Soc., 1939, 16, 19—26; cf. A., 1937, II, 200).—Camphor and Na·Et₂O-*p*-NMe₂·C₆H₄·CHO at <5° give *p*-dimethylaminobenzylidenecamphor, m.p. 141—141.5°, [α]_D +731° in EtOH (cf. [α]_D +425° for benzylidenecamphor). HCl causes a fall in [α], *e.g.*, to 343°, and a little MeI in MeOH from 704.6° to 621°, possibly owing to ionisation of the quaternary salt. *p*-Dimethylamino-anilocamphor has [α]_D +2487° in EtOH (cf. +726° for NH₂-compound) and -benzylidene-β-hydroxynaphthylbenzylamine, [α]_D +704° in C₆H₆ (cf. +59° for NH₂-compound). Rotatory powers of *o*-diethyl-, m.p. 151—153° (shrinks at 147°), and *o*-dimethyl-aminocamphoranilic acid (*loc. cit.*)

rise considerably on addition of HCl, *e.g.*, the former from [α]_D +5° to +39° in MeOH, +2° to +20° in EtOH, —12.3° to +7.6° in COMe₂, and the latter from 0° to +55° (MeOH), +51° (EtOH). Camphoric anhydride and the respective NR₂·C₆H₄·NH₂ give the following; approx. vals. of [α]_D are given in MeOH, EtOH, COMe₂, respectively and figures in parenthesis are vals. after adding HCl: *p*-methyl-*p*-ethyl-, m.p. 179—180°, [α]_D +60.6° (+62.5°), +54.6° (+58.2°), +47.8°, *p*-diethyl-, m.p. 170.5—171°, [α]_D +83.8° (+91.7°), +78.2° (+86.2°), +85.7°, *p*-dipropyl-, m.p. 180.5°, [α]_D +44.5°, 51.9°, 43.9°, *p*-dibutyl-, m.p. 112—113°, [α]_D +55.4° (+64.4°), +72.7°, +60.0°, -aminocamphoranilic acids. *d*-Hydroxymethylencamphor and the respective *p*-NR₂·C₆H₄·NH₂ in MeOH-aq. AcOH afford *p*-dimethyl-, m.p. 173—173.5° (darkens at 169°), [α]_D +339.7° (+244.6°), +305°, +340°, *p*-methyl-*p*-ethyl-, m.p. 132—132.5° (darkens at 126.5—128°), [α]_D +333.5° (+240.3°), +330°, 330°, *p*-diethyl-, m.p. 134.5—135°, [α]_D +303.8° (+221.3°), +316°, +375°, *p*-dipropyl-, m.p. 136.5—137° (darkens at 128—129°), [α]_D +326.3° (+291°), +336°, +315°, and *m*-dimethyl-, m.p. 159.5—160°, [α]_D +322°, +340°, +342° (+375°), -aminoanilinomethylenecamphor. Vals. of [α]_D in other solvents, *e.g.*, COMeEt, CHCl₃, are recorded.

A. T. P.

Structure of origanene. II. Its identity with α-thujene. A. J. BIRCH and J. C. EARLE (J. Proc. Roy. Soc. New South Wales, 1939, 72, 55—61; cf. A., 1939, II, 170).—Origanene (I) is a mixture of *d*- and *dl*-α-thujene; the latter affords a nitrosochloride identical with that obtained by Pickles (J.C.S., 1908, 93, 868); difference in physical consts. is attributed to α-terpinene in that from the latter source. The physical consts. of (I) from *Eucalyptus dives* oil are compared with those of allied products obtained by Tschugaev *et al.* (A., 1912, i, 479) and Simonsen (A., 1923, i, 693) from other sources; the latter types probably contain *d*-β-thujene (cf. also Henry *et al.*, A., 1931, 357). The identity of (I) is confirmed by conversion of the dibromide into *p*-cymene by C₅H₅N, and the formation of terpinene dihydrochloride by HCl-AcOH. (I) and KMnO₄-COMe₂ gives a cryst. α-thujaketonic acid, m.p. 75—76°, and a liquid *dl*-α-thujaketonic acid (semicarbazone, m.p. 196—197°, is identical with that from either *d*- or *l*-α-thujaketonic acid) and a little pinonic acid. When distilled under reduced pressure, both cryst. and liquid forms above give β-thujaketonic acid. A. T. P.

Constitution of caryophyllene. II. Oxidation reactions of caryophyllene and dihydrocaryophyllene. H. N. RYDON (J.C.S., 1939, 537—540).—Oxidation of dihydrocaryophyllene (I) with H₂SeO₃ gives *dihydrocaryophyllene aldehyde*, b.p. 157—160°/15 mm. (*semicarbazone*, m.p. 242°), and with BzO₃H yields a mixture of *dihydrocaryophyllene α*-, b.p. 134—137°/12 mm., α_D²⁰ —3.38°, and β-oxide, b.p. 145—147°/12 mm., α_D²⁰ —4.46°. The formation of the two oxides suggests that (I) is a mixture, derived from the two non-conjugated caryophyllene isomerides and the conjugated isomeride, respectively (cf. A., 1938, II, 107). Oxidation of caryophyllene with H₂SeO₃ gives only resinous products but with

BzO₂H, *caryophyllene oxide*, b.p. 138—141°/10 mm., is obtained.

F. R. S.

Constitution of β -caryophyllene. G. R. RAMAGE and J. L. SIMONSEN (Chem. and Ind., 1939, 447).—*Dimethylamino- β -caryophyllene* [prep. from the NH₂-compound (A., 1935, 90), b.p. 154°/12 mm., and KMnO₄-H₂SO₄] gives a *ketone* (I), C₁₆H₂₀ON, b.p. 170—175°/12 mm., and an *acid* (II), C₁₄H₂₀O₂N (*Me* ester, b.p. 175—180°/12 mm.). This confirms the structures of Ruzicka for β -caryophyllene, refutes those of Rydon (A., 1938, II, 107) and suggests the structure $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}$
 $\text{CH}_2\cdot\text{CH}\cdot\text{CHR}\cdot\text{CH}\cdot\text{NMe}_2$ [(I), R = CH₂·CMe; (II), R = CO₂H].

R. S. C.

Ketones from the vetiver oil. S. SABETAY and L. TRABAUD (Bull. Soc. chim., 1939, [v], 6, 740—743).—Bourbon (or Java) vetiver oil, refluxed with EtOH-AcOH (Girard reagent P) for 1 hr., affords a ketone, *vetiverone*, C₁₅H₂₂O, b.p. 142—150°/12 mm., purified through the *semicarbazone*, m.p. 210°. Vetiverol and Na₂Cr₂O₇ in aq. H₂SO₄ give *vetiveraldehyde*, b.p. 138—145°/10 mm.

A. T. P.

Caoutchicol. E. R. H. JONES (Chem. and Ind., 1939, 446).—Caoutchicol (A., 1939, II, 212) and lupeol (A., 1938, II, 23, 195) are identical (m.p. and m.p. of derivatives; mixed m.p.). The latter name is preferred.

R. S. C.

Precursor of Buckley's compound. S. H. HARPER (Chem. and Ind., 1939, 292).—Et₂O extractions of *Derris elliptica* root, when freed from toxicarol and rotenone and dissolved in Et₂O, deposited *elliptone* (I), C₂₀H₁₆O₅, m.p. 159°, $[\alpha]_D^{20}$ -18° in C₆H₆, which, when racemised by hot NaOAc-EtOH, yields Buckley's substance (II), m.p. 176°. (I) is thus the precursor of (II), which is not formed by decomp. of deguelin (cf. Harper, A., 1938, II, 503; Cahn *et al.*, A., 1939, II, 33).

R. S. C.

Constitution of pine lignin. K. FREUDENBERG and W. LAUTSCH (Naturwiss., 1939, 27, 227—228).—The nature of the structural unit of pine lignin is discussed in the light of degradation experiments.

A. Li.

Lignin and related compounds. XXXVIII. Effect of solvents in the Grignard analysis for active hydrogen and carbonyl. M. LIEFF, G. F. WRIGHT, and H. HIBBERT. XXXIX. Ethanolysis of spruce and maple woods. L. BRICKMAN, J. J. PYLE, P. L. MCCARTHY, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 865—867, 868—869; A., 1939, II, 221).—XXXVIII. Various compounds give more nearly quant. results with MgMeI in C₅H₅N than in dioxan or xylene. 3:4-(OMe)₂C₆H₃·CHO shows active H at the expense of CO in dioxan or C₅H₅N, probably owing to benzoin formation. Benzoin, its acetate and *formate*, m.p. 73—74°, react partly as dienols in dioxan or C₅H₅N, but the esters react normally in xylene. The amount of enol shown by CPhR varies with the solvent. *o*-C₆H₄(OAc)₂ reacts normally and completely in xylene, but shows active H (? reason) in C₅H₅N.

XXXIX. The yield of H₂O-sol. products obtained by ethanolysis of various lignins is greatly increased by extracting the products with C₆H₆ in CO₂; nearly

complete absence of acids shows that they were formed by oxidation of the primary products in earlier experiments.

R. S. C.

Preparation and properties of (I) *l*-abietic acid and (II) *d*-abietic acid. G. A. GARKUSCHA (J. Gen. Chem. Russ., 1938, 8, 1042—1052, 1053—1061).—I. The purest sample of *l*-abietic acid obtained from colophony by a variety of methods had $[\alpha]_D^{20}$ -111° in EtOH, and is probably a mixture of stereoisomerides.

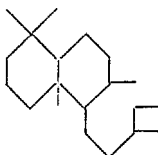
II. The purest *d*-abietic acid obtained had $[\alpha]_D^{20}$ +56.8° in EtOH, and is also a mixture of stereoisomerides.

R. T.

Hydration of dihydropimaric acid. T. HASSELMAN and B. L. HAMPTON (J. Amer. Chem. Soc., 1939, 61, 967—968).—Dihydropimaric acid, m.p. 241—243° (corr.), $[\alpha]_D^{20}$ +19.2° [*Me* ester, m.p. 78.5—79.5° (corr.)], and conc. H₂SO₄ at 5° give a *lactone*, C₂₀H₃₂O₂, m.p. 143—144° (corr.), $[\alpha]_D^{20}$ -40° in EtOH, hydrolysed by 10% KOH-BuOH but thereafter reconverted into the *lactone* by acid.

R. S. C.

Marrubiin, the bitter principle of horehound (*Marrubium vulgare*). A. LAWSON and (MISS) E. D. EUSTICE (J.C.S., 1939, 587—589).—The formula, C₂₀H₂₈O₄, and not C₂₁H₂₈O₄ (cf. Gordin, A., 1908, i, 344), is suggested for marrubiin (I), and is supported by the isolation of 1:2:5-C₁₀H₅Me₃ from the Se-dehydrogenation products of (I). Marrubic acid, m.p. 205° (decomp.) (lit. 173—174°), forms an *Ac* derivative (+H₂O), m.p. 112°. Hydrogenation in AcOH (PtO₂) gives *tetrahydromarrubiin*, m.p. 134°, in 60% yield; it is concluded that two double linkings are present in the cyclic part of the structure. The H₄-derivative with HCl yields a *substance*, C₂₀H₃₀O₃, m.p. 124°, hydrogenated to a *substance*, C₂₀H₃₂O₃, m.p. 89°. PCl₃ and (I) afford a *substance*, C₂₀H₂₆O₃, m.p. 98°, hydrogenated to a *product*, C₂₀H₃₂O₃, m.p. 106°, which is hydrolysed to an *acid*, C₂₀H₃₄O₄, m.p. 210°. (I) is probably a diterpene *lactone* and the C skeleton is suggested.



(I)

F. R. S.

Soya-bean saponins. V. K. TSUDA and Z. ICHIKAWA (Ber., 1939, 72, [B], 716—723; cf. A., 1938, II, 239, 416).—Hydrogenation (Cu-Cr oxide in cyclohexane at 250—260°/150 atm.) of methyl-hederagenin gives *dehydroxymethylhederagenin* (I), C₃₀H₄₈O₃, m.p. 185°, $[\alpha]_D^{20}$ +102.58° in CHCl₃. The *monoacetate*, m.p. 172°, is transformed by Br in MeOH at room temp. into the *monobromide*, C₃₂H₄₉O₄Br, m.p. 217°, and absorbs 1 O from BzO₂H in CHCl₃. (I) is transformed by Cu-bronze at 270—290° followed by distillation in a high vac. into methyl-hedragone (II), m.p. 203° (*monosemicarbazone*, m.p. 221°). The pressure hydrogenation of soya-sapogenol B (III) follows a similar course, leading to a *compound* (IV), C₃₀H₄₈O₂, m.p. 240—242°, $[\alpha]_D^{20}$ +113.6° in CHCl₃ (*diacetate*, m.p. 208—210°); it is dehydrogenated by Cu-bronze at 280° and distillation to the *diketone* (V), C₂₉H₄₄O₂, m.p. 252—254° (*dioxime*, decomp. 270°), obtained by the direct dehydrogenation of (III). Somewhat different results are obtained by the pressure hydrogenation of (II), which

gives the following substances: (a) $C_{30}H_{48}O_2$, m.p. 181—183°, which contains 1 OMe and is also obtained by reduction (Clemmensen) of (II); (b) $C_{30}H_{48}O_3$, m.p. 185°, identical with (I); (c) $C_{29}H_{48}O_2$, m.p. 197°, which gives a diacetate, m.p. 194°, and is isomeric with (IV). Hydrogenation (PtO_2 in AcOH) of (II) and treatment of the product with NaOAc and boiling Ac_2O gives an acetate, $C_{30}H_{48}O_3Ac$, m.p. 190—191°, isomeric with the product from (I). Hydrogenation (Cu—Cr oxide in cyclohexane at 270°/160 atm.) of (V) affords (IV) and a hydrocarbon, $C_{29}H_{48}$, m.p. 153°. Reduction (Clemmensen) of (V) yields an isomeric hydrocarbon, m.p. 160°, whereas hydrogenation (PtO_2 in AcOH) gives a diol (diacetate, $C_{29}H_{46}O_2Ac_2$, m.p. 166—167.5°). H. W.

Scission of hydrofuran and hydropyran rings with acetic anhydride. R. PAUL (Compt. rend., 1939, 208, 587—589).—Tetrahydropyran when heated (>190°) with Ac_2O — $ZnCl_2$ affords only $CH_2(CH_2CH_2OAc)_2$ (23%). 2-Methyl-, -propyl-, and -butyl-tetrahydropyran similarly give 24%, 10%, and 11% yields of the corresponding α -(OAc) $_2$ -compounds, as well as 70%, 84%, and 83% of unsaturated OAc-compounds. 2-Phenyltetrahydropyran resinifies under these conditions. 2-Ethyl- (I), -butyl- (II), -amyl- (III), -benzyl- (IV), -carboethoxy-, - β -carbethoxyethyl-, -carbomethoxymethyl-, - α -carbomethoxyethyl-, and - α -carbomethoxypropyl-tetrahydrofuran similarly afford 22, 18, 15, 29, 57, 56, 74, 67, and 89% of the corresponding $\alpha\delta$ -(OAc) $_2$ -derivatives. (I), (II), (III), and (IV) afford in addition 64, 76, 77, and 20% of unsaturated OAc-compounds. Tetrahydrofuran affords only $(CH_2CH_2OAc)_2$ (77%). The tetrahydrofuran ring is the more easily opened, probably owing to the strain at the O. 2-Substituents with electron-donating properties tend to yield the diacetate rather than the ethylenic compounds. The less marked is the polarity of the substituent the greater is the tendency to give the unsaturated compound. J. L. D.

Electrochemical reduction of furfural. W. C. ALBERT and A. LOWRY (Trans. Electrochem. Soc., 1939, 75, Preprint 20, 245—252).—Reduction of furfuraldehyde (I) in 10% KH_2PO_4 with a Pb cathode, at c.d. 0.005 amp. per sq. cm., for 16 hr. at 18—25° gives, in addition to furfuryl alcohol and resin, a 63% yield of a mixture of *hydrofuroin* and *isohydrofuroin*, $C_4H_7O \cdot [CH(OH)]_2 \cdot C_4H_7O$, b.p. 135°/1 mm., one isomeride having m.p. 64—65° (Ac_2 , m.p. 67—68° and 112—113°, and Bz_2 , m.p. 94—95° and 180°, derivatives), and giving (I) on oxidation with $Pb(OAc)_4$. The effects of varying the material of the cathode, temp., c.d., and p_H are recorded. F. R. G.

Synthesis of ketones of the furan series. J. L. GOLDFARB and L. M. SMORGONSKI (J. Gen. Chem. Russ., 1938, 8, 1523—1526).—Furan in C_6H_6 and acid anhydrides or chlorides in presence of $SnCl_4$ at room temp. (12—18 hr.) yield furyl ketones, of which the following appear to be new: *furyl Me*, b.p. 174—175°, m.p. 29°, *Et*, b.p. 74—75°/16 mm., *Pr*, b.p. 88°/14 mm., and *Ph ketone*, b.p. 146—147°/10 mm. R. T.

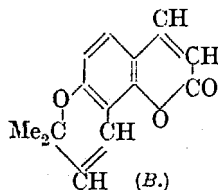
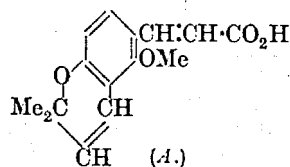
Furan amines.—See B., 1937, 522.

Constituents of *Didymo-carpus pedicellata*. II. Constitution of pedicin, isopedicin, pedicinin, and pedicellin. V. SHARMA and S. SIDDIQUI (J. Indian Chem. Soc., 1939, 16, 1—8; cf. A., 1938, II, 196).—Pedicin (I) and pedicellin (II) are 5:6-dihydroxy-2:3:4-trimethoxy- and 2:3:4:5:6-pentamethoxy-(phenylhydrazono, m.p. 133—135°; Br_2 -derivative, m.p. 132°)-phenyl styryl ketone, respectively. (I) and Me_2SO_4 —NaOH give (II). Pedicinin (III) and isopedicin (IV) are 4:5:7-trihydroxy-3-keto-6-methoxy-2-benzylidene-benzo- and 7-hydroxy-3-keto-4:5:6-trimethoxy-2-benzyl-2:3-dihydrofuran, respectively. (I), (II), or (III) and HI (d 1.77) at 130—140° give 2:3:4:5:6-pentahydroxyphenyl styryl ketone ("des-pedicellin"), m.p. 255—256° (decomp.) (shrinking and partial sublimation at 230°) (phenylhydrazono, m.p. 196°). (I) or (II), when heated with aq. NaOH, or oxidised (H_2O_2 or $KMnO_4$), gives $PhCHO$ and an (?) acid. (I) and $KMnO_4$ —aq. NaOH (ice) give $PhCHO$ and (III). (IV) and 30% aq. NaOH at room temp. afford (I). (II) and HNO_3 (d 1.4)—AcOH give a dihydroxydimethoxy-3-keto-2-benzylidenebenzo-2:3-dihydrofuran, m.p. 110°, demethylated (aq. NaOH) at room temp. to (III). Colour reactions of (III) and formation by aq. NaOH of $PhCHO$ exclude a flavone or isoflavone structure. (I) and 2 atoms of Br in $CHCl_3$ in the cold give (III) [mechanism discussed]; 4 equivs. of Br give a Br_2 -derivative, m.p. 180° (decomp.), of (III). Dibenzoyl- (or dimethyl-)pedicin, however, affords a Br_2 -derivative, m.p. 170° (decomp.). Hydrogenation of (I) (Pt -black—MeOH) gives a H_2 -derivative, m.p. 120—121°. The structures of the above compounds are not allied to that of duniione (cf. A., 1938, II, 375). A. T. P.

Vitamin-E. VI. Synthesis of lower homologues of α -tocopherol. (Miss) A. JACOB, (Miss) M. STEIGER, A. R. TODD, and T. S. WORK (J.C.S., 1939, 542—545).—*p*-Xyloquinol and CH_2PhCl give a mixture of *p*-xyloquinol di-, m.p. 130°, and mono-benzyl ether, m.p. 92—93°, and a violet substance, $C_{23}H_{24}O_4$, m.p. 111—112°. *o*-Xyloquinol similarly yields di-, m.p. 109°, and mono-benzyl ethers, m.p. 116°, but no coloured compound. Condensation of the monobenzyl ethers with phytol bromide (I) affords oils showing vitamin-E activity but difficult to purify. Benzoylation and acetylation lead to *p*-xyloquinol di-, m.p. 159°, and mono-benzoate (II), m.p. 162—163°, *o*-xyloquinol di-, m.p. 182°, and mono-benzoate (III), m.p. 174—175°, and *p*-xyloquinol di-, m.p. 135°, and mono-acetate, m.p. 117°. Condensation of (II) with phytol or (I), followed by hydrolysis of OBz, gives a tocopherol [6-hydroxy-2:5:8-trimethyl-2-(4':8':12'-trimethyltridecyl)chroman], forming a *p*-nitrophenylurethane, m.p. 111—112°. Similar condensation of (III) and (I) gives the tocopherol (2:7:8- Me_3 compound) (*p*-nitrophenylurethane, m.p. 100°). These compounds show biological activity comparable with that of β - and γ -tocopherol. The crude tocopherol obtained from *m*-xyloquinol and phytol forms a *p*-nitrophenylurethane, m.p. 89°, and appears to have an activity approaching that of α -tocopherol (cf. Karrer *et al.*, A., 1939, II, 174). F. R. S.

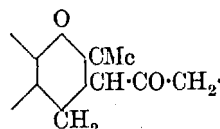
Egonol. General synthetical method for 2-phenylcoumarone and its derivatives and synthesis of egonol. S. KAWAI, T. NAKAMURA, and N. SUGIYAMA (Proc. Imp. Acad. Tokyo, 1939, 15, 45—48).— $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and $\text{CHPhBr}\cdot\text{CO}_2\text{Et}$ give (K_2CO_3) *Et* 3-hydroxy-2-phenylcoumaran-2-carboxylate, m.p. 116°, hydrolysed to the acid, decomp. 99.5°, which is decarboxylated to 2-phenylcoumarone. Similarly, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ and *Et* α -chloro-3:4-methylenedioxyphenylacetate (I) yield *Et* 3-hydroxy-2-(3':4'-methylenedioxyphenyl)coumaran-2-carboxylate, m.p. 146°, and an isomeric oily ester, both of which afford the corresponding acid, decomp. 177°, decarboxylated to 2-(3':4'-methylenedioxyphenyl)coumarone, m.p. 102—102.5°. Styranilic aldehyde and (I) give the coumarane ester derivative, hydrolysed and decarboxylated to a substance, which after purification through its Ac derivative, is identical with natural egonol [7-methoxy-5-(ω -hydroxy-*n*-propyl)-2-(3':4'-methylenedioxyphenyl)coumarone]. F. R. S.

Coumarins of *Seseli indicum* and the constitution of seselin. E. SPÄTH, P. K. BOSE, J. MATZKE, and N. C. GUHA (Ber., 1939, 72, [B], 821—830).—The isolation of seselin (I), m.p. 119—120°, bergapten, and isopimpinellin from the seeds of *S. indicum* is fully described. (I), $\text{C}_{14}\text{H}_{12}\text{O}_3$, does not contain OH or OMe. It does not react with the customary reagents for CO. It contains two double linkings which are hydrogenated stepwise (Pd-sponge in AcOH to di-, m.p. 104—105°, and tetra- (II), m.p. 106—107°, -hydroseselin. (I) is hydrolysed by hot 5% KOH to a yellow solution from which it is regenerated on acidification. KMnO_4 oxidises (II) to succinic acid but H_2O_2 does not yield a furan-2:3-dicarboxylic acid, thus showing the absence of a coumarone ring. Under the usual conditions (I) is unaffected by $\text{H}_2\text{SO}_4\text{-AcOH}$ so that it is not a prenyl ether; with more of H_2SO_4 , (I) is converted into umbelliferone. Energetic ozonisation of (I) gives COMe_2 as volatile product whilst the use of less O_3 leads to resorcinol-2:4-dialdehyde. Oxidation (KMnO_4) of (I) in alkaline solution gives $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Hydrolytic methylation of (I) affords the acid A, m.p. 97—98°, oxidised and methyl-



ated (CH_2N_2) to Me_2 2-methoxy-4- α -carbomethoxyethoxyisophthalate (II), m.p. 82—83°, which contains 4 OMe. (I) is therefore B. 7-Hydroxycoumarin-8-aldehyde is converted by NaOMe in MeOH into the Na derivative, which is transformed by $\text{CMe}_2\text{Br}\cdot\text{CO}_2\text{Me}$ at 100° into 7- α -carbomethoxy- α -methylethylcoumarin-8-aldehyde, m.p. 170—171°; this is converted by treatment with Me_2SO_4 and NaOH followed by oxidation with KMnO_4 and treatment with CH_2N_2 into (II). H. W.

Rottlerin. V. H. S. BAKSHI, R. S. JALOTA, K. S. NARANG, and J. N. RAY (Current Sci., 1939, 8, 165—166).—*iso*Rottlerin (I) (Brockmann and Maier, A., 1938, II, 334) is identical with the colouring matter, m.p. 181°, of Narang *et al.* (A., 1938, II, 66). Separation of (I) from rottlerin (II) is best effected chromatographically. The Me ether of (I) has m.p. 135°, not 105° (*loc. cit.*), and gives [unlike (II)] a piperonylidene derivative, m.p. 145—147°, an oxide (with H_2O_2), m.p. 120—122°, and a nitrosite, m.p. 194—197°. Hydrogenation gives a substance, $\text{C}_{31}\text{H}_{32}$ or C_{31}O_8 , m.p. 209°, and a by-product, $(\text{C}_{11}\text{H}_{12}\text{O}_3)_n$, m.p. 225—228°. (I) is considered to contain the structure



F. R. G.

Amino- and hydroxy-derivatives of dibenzfuran. L. C. CHENEY (Iowa State Coll. J. Sci., 1938, 13, 57—59).—The following new compounds which were described in a thesis are listed: 1:8-dihydroxy-, m.p. 200—202° [(OMe)₂-derivative (I), m.p. 128—129° (picrate, m.p. 161—162°)], 2-hydroxy-, m.p. 174—175°, and 8-amino-1:2:3:4-tetrahydrodibenzfuran [hydrochloride, m.p. 227—228° (decomp.)]; di-1-dibenzfuryl, m.p. 191°, and di-1-(1-methoxydibenzfuryl) ketone, m.p. 234°; di-4-(1-methoxydibenzfuryl) (II), m.p. 329°, and di-4-(1:8-dimethoxydibenzfuryl) (III), m.p. >300°; 4-chloroacetyl-1-methoxy- (IV), m.p. 165—166°, and 4-ethoxalyl-1-methoxy-dibenzfuran, m.p. 113°; 1-methoxy-4-dibenzfurylhydroxyacetic acid, m.p. 187° [semicarbazone, m.p. 211—212° (decomp.)]; 2-hydroxy-1-methoxydibenzfuran, m.p. 109—110° (OMe-derivative, m.p. 60—61°); di-1-(8-hydroxydibenzfuryl), m.p. 285—286° [(OMe)₂-derivative, m.p. 237—238°]; 1:2-dihydroxy-, m.p. 164—164.5°, 1-bromo-8-hydroxy-, m.p. 138—139° (OMe-derivative, m.p. 114°), 1-amino-8-hydroxy-, m.p. 191.5—192.5° (OMe-derivative, m.p. 109°), 4-bromo-2-hydroxy-1-methoxy-, m.p. 161—162° (OMe-derivative, m.p. 108°), 4-bromo-1:8-dimethoxy-, m.p. 152°, 4:5-dibromo-1:8-dihydroxy-, m.p. 239—240° [(OMe)₂-derivative, m.p. 167—168°], 2:4(?) dibromo-1-hydroxy-8-methoxy-, m.p. 177—178° (OMe-derivative, m.p. 173.5—174°), 1:3-diamino-, m.p. 152° [picrate, m.p. 213° (decomp.)]; Ac₂ derivative, m.p. 297—298°, 1:8-diacetoxy-, m.p. 177°, 1:2-diacetoxy-, m.p. 104—105°, 4-acetyl-1:8-dimethoxy-, m.p. 178—179.5° (oxime, m.p. 203—204°), 4-acetyl-1:2-dimethoxy-, m.p. 90.5—91° (oxime, m.p. 156—157°), 4-benzeneazo-1-hydroxy-8-methoxy-, m.p. 175° (OMe-derivative, m.p. 170°), 4-amino-1:8-dimethoxy-, m.p. 162—162.5° [Ac derivative (V), m.p. 244—245°], and 4-amino-1:2-dimethoxy-dibenzfuran, m.p. 162.5—163° (Ac derivative, m.p. 196—196.5°); 1:8-dimethoxydibenzfuran-4-carboxylic acid, m.p. 297—298° (Me ester, m.p. 163°); diazomethyl 1:8-dimethoxy-4-dibenzfuryl ketone, m.p. 151° (decomp.); 1:8-dimethoxy-4-dibenzfurylacetic acid, m.p. 205—206° (amide, m.p. 210—211°); 2:4:5-tri-benzeneazo-1:8-dimethoxydibenzfuran, m.p. 191—193°; and di-4-(1:8-dimethoxydibenzfuryl) ketone, m.p. 254—255°.

(IV) is not cyclised by the Friedel-Crafts reaction. 1-Methoxydibenzfuran and (I) with $(\text{COCl})_2\text{-AlCl}_3$ yield (II) and (III), respectively. (V) is not cyclised by the Bischler-Napieralski reaction. J. L. D.

Dibenzfuran. IX. Metallation of some derivatives. H. GILMAN, L. C. CHENEY, and H. B. WILLIS. **X. Aminohydroxy-derivatives.** H. GILMAN, A. L. JACOBY, and J. SWISLOWSKY (J. Amer. Chem. Soc., 1939, **61**, 951—954, 954—956).—IX. Metallation of dibenzfurans containing an OR occurs *o*- to the OR. Dibenzfuran with LiBu^a , followed by $\text{MgBu}^a\text{-Br}$ and then O_2 , gives 1-hydroxydibenzfuran (40—52.5%) and di-1-dibenzfuryl (I), m.p. 191°. 1-Methoxydibenzfuran (II) gives similarly 4-, m.p. 111—112°, and 2-hydroxy-1-methoxydibenzfuran, m.p. 109—110° (also obtained by boiling diazotised 2-amino-1-methoxydibenzfuran with aq. CuSO_4). Treating (II) first with LiBu^a at -10° and then with Br in N_2 at 0° gives 1-bromo-8-methoxydibenzfuran (7.3%), m.p. 114°, and probably also the 2-Br-compound. The Grignard reagent from 1-bromo-7-methoxydibenzfuran with anhyd. CuCl_2 gives 61.5% of di-8-methoxy-1-dibenzfuryl, m.p. 237—238°, converted by HBr-AcOH into the 8:8'-(OH) $_2$ compound, m.p. 285—286°. 3-Bromodibenzfuran (III) with LiBu^a , followed by CO_2 , gives 3-bromodibenzfuran-1-carboxylic acid, m.p. 285—286° (*Me* ester, m.p. 189—189.5°), and some dibenzfuran [probably formed by reaction of (III) with Li 3-dibenzfuryl]. $\text{H}_2\text{-Pd-CaCO}_3$ converts (IV) into the known dibenzfuran-1-carboxylic acid. With LiBu^a , followed by Me_2SO_4 , (III) gives a mixture, containing 3-bromo-1-methyl-dibenzfuran. (See preceding abstract.)

X. 1-Acetamidodibenzfuran and HNO_3 (*d* 1.49) in Ac_2O at -10° give the 2- NO_2 -derivative (I), m.p. 238° (other conditions give the 4- NO_2 -derivative), hydrolysed by HCl-EtOH to 2-nitro-1-aminodibenzfuran (II), m.p. 185—186°, which by diazotisation and treatment with $\text{H}_2\text{SO}_4\text{-EtOH}$ gives 2-nitrodibenzfuran. Catalytic hydrogenation of (I) gives 2-amino-1-acetamidodibenzfuran, m.p. 236—237°, and thence by $\text{Ac}_2\text{O-C}_6\text{H}_6$ the 1:2-(NHAc) $_2$ -derivative, m.p. 257°. Hydrogenation (Raney Ni; EtOH) of (II) gives the unstable diamine, which with phenanthraquinone gives dibenzo[a, c]benzofuro[2:3-h]phenazine, m.p. 277—278°. Boiling diazotised (II) in $\text{H}_2\text{SO}_4\text{-CuSO}_4\text{-H}_2\text{O}$ gives 2-nitro-1-hydroxydibenzfuran (III), m.p. 193°, also obtained from 1-hydroxydibenzfuran by HNO_3 (*d* 1.5) in Ac_2O at -12° , and converted by CH_3N_2 into 2-nitro-1-methoxydibenzfuran, m.p. 129.5°. $\text{H}_2\text{-Raney Ni}$ in EtOH then gives 2-amino-1-methoxydibenzfuran, m.p. 75.5° (hydrochloride, m.p. $>230^\circ$). 1-Hydroxydibenzfuran and conc. HNO_3 in AcOH at 60° give the 2:6-(NO_2) $_2$ -derivative, m.p. 225° (decomp.), also obtained similarly from (III) and converted by CH_3N_2 into 2:6-dinitro-1-methoxydibenzfuran, m.p. 177°. 2-Hydroxydibenzfuran gives similarly the (? 2:6-)(NO_2) $_2$ -derivative, m.p. 240° (decomp.). 1-Methoxydibenzfuran and fuming HNO_3 in Ac_2O at -15° to -20° give the 4- NO_2 -derivative, m.p. 155°, and thence ($\text{H}_2\text{-Raney Ni}$) 4-amino-1-methoxydibenzfuran, m.p. 104° (hydrobromide, m.p. $>250^\circ$; hydrochloride), also obtained from 4-bromo-1-methoxydibenzfuran, aq.

NH_3 , and CuBr at 230—240°. 4-Nitro-1-ethoxydibenzfuran (prep. from the phenol by $\text{Et}_2\text{SO}_4\text{-NaOH}$), m.p. 135—135.5°, yields ($\text{H}_2\text{-Raney Ni}$) 4-amino-1-ethoxydibenzfuran, m.p. 91° (hydrochloride; *Ac* derivative, m.p. 218.5°). 2-Aminodibenzfuran, EtI , and hot aq. K_2CO_3 give 2-diethylaminodibenzfuran, m.p. 68°. R. S. C.

Decolorisation of fluorescein. V. BRUSTIER, P. VALDIGUIÉ, and P. BLANC (Bull. Soc. chim., 1939, [v], **6**, 548—550).—Both colour and fluorescence of dil. solutions of the Na_3 salt are removed by $\text{NaOCl} + \text{dil. acid}$, or by $\text{KMnO}_4\text{-HCl}$ (or H_2SO_4)- H_2O_2 . The absorption spectrum shows that the product formed probably has a lactone structure. A. LI.

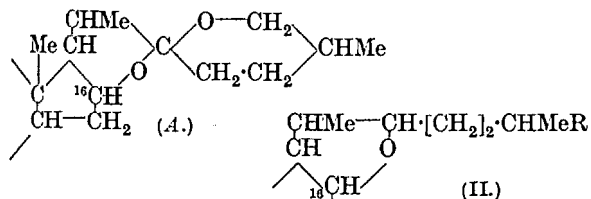
Pigments of cotton flowers. VI. Methylation of herbacetin. S. RANGASWAMI, P. S. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, **9**, A, 133—135).—Herbacetin and CH_3N_3 in $\text{MeOH-Et}_2\text{O}$ give the 3:7:8:4'-*Me* $_4$ ether, $+2\text{H}_2\text{O}$ (1.5 H_2O lost at 120°), sinters at $120\text{--}125^\circ$, m.p. $159\text{--}160^\circ$, or $+0.5\text{H}_2\text{O}$, m.p. $160\text{--}162^\circ$, which with $\text{Me}_2\text{SO}_4\text{-KOH}$ in aq. COMe_2 gives the Me_5 ether, $+3\text{H}_2\text{O}$ (Goldsworthy *et al.*, A., 1938, II, 110). R. S. C.

Compounds of the $\alpha\beta$ -dinaphtha- γ -pyrone type. K. DZIEWOŃSKI and T. CHOMIK (Bull. Acad. Polonaise, 1938, A, 541—550).— $\alpha\beta$ -Dinaphtha- γ -pyroneanil [bis(naphtha-1':2')-3:2:5:6- γ -pyroneanil] (modified prep.), m.p. 263—265°, and 3% Na-Hg in hot EtOH give 4-anilinobis(naphtha-1':2')-3:2:5:6- γ -pyran, m.p. 189—190° [pyrylium nitrate, m.p. 175—176° (decomp.)], and some bis(naphtha-1':2')-3:2:5:6- γ -pyran, m.p. 202°. 1:6- $\text{C}_{10}\text{H}_6\text{Me.OH}$ and CS(NHPh)_2 , first at 250° and then at 265° , give bis-(5'-methylnaphtha-1':2')-3:2:5:6- γ -pyroneanil, m.p. 234—235°, reduced by Na-Hg in EtOH to 4-anilinobis-(5'-methylnaphtha-1':2')-3:2:5:6- γ -pyran, m.p. 219° (pyrylium salts), and hydrolysed by HCl-AcOH to bis-(5'-methylnaphtha-1':2')-3:2:5:6- γ -pyrone (I), m.p. 232°. 3% Na-Hg in hot EtOH reduces (I) to bis-(5'-methylnaphtha-1':2')-3:2:5:6- γ -pyran (II), m.p. 266° (pyrylium picrate, m.p. 170—172°), and - γ -pyranol, m.p. 196.5° [pyrylium nitrate, m.p. 176—177° (decomp.)], converted by hot EtOH into (II)]. 2:6- $\text{C}_{10}\text{H}_6\text{Me.OH}$ and CS(NHPh)_2 , first at 150° and then at 265° , give similarly bis-(6'-methylnaphtha-1':2')-3:2:5:6- γ -pyroneanil, m.p. 192—194°, and thence by the above methods 4-anilinobis-(6'-methylnaphtha-1':2')-3:2:5:6- γ -pyran, m.p. 212°, bis-(6'-methylnaphtha-1':2')-3:2:5:6- γ -pyrone, m.p. 241—242°, and - γ -pyranol (III), m.p. 294°. Dil. HCl and (III) give the pyrylium chloride hydrochloride, m.p. 197—199°, converted by hot EtOH into bis-(6'-methylnaphtha-1':2')-3:2:5:6- γ -pyran, m.p. 234—235°.

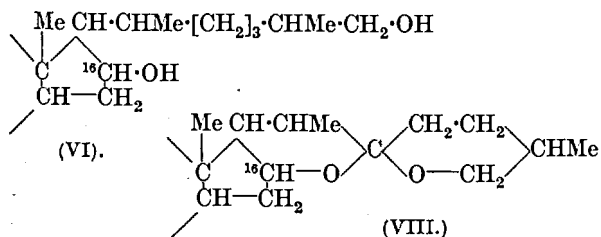
R. S. C.

Sterols. LIII. Structure of the side-chain of sarsasapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, **61**, 846—851).—Sapogenins are very reactive in acid solution and probably contain the structure (A). Hydrogenation (PtO_2) of sarsasapogenin acetate (I) in AcOH (at $70^\circ/3$ atm.), AcOH-EtOH (4:1) or HCl-EtOH (at room temp./3 atm.) (not in neutral solution) gives a

product, hydrolysed by KOH-EtOH to *dihydrosarsasapogenin* [(II), R = CH₂·OH], m.p. 165° (*bis*-



3:5-dinitrobenzoate, m.p. 220°), which forms a digigitonide and thus contains a 3-β-OH; retention of the C₁₆ oxide ring follows from resistance of tetrahydrofurfuryl acetate (III) to hydrogenation in acid solution. CrO₃-AcOH oxidises (II), (R = CH₂·OH) to 3-ketosarsasapogentic acid, C₂₇H₄₂O₄ [(II), R = CO₂H; CO at C₁₃], m.p. 198° [semicarbazone, m.p. 180° (decomp.); positive Zimmermann reaction], which proves the CH₂·OH. Hydrogenation of (I), oxidation of the crude H₂-acetate, and hydrolysis by hot 3% aq. NaOH affords *sarsasapogentic acid* [(II), R = CO₂H; OH at C₁₃], m.p. 187° (digitonide; Me ester, m.p. 124°). Attempts to reduce sarsasapogenin (IV) by Al(OPrⁱ)₃ or Na-C₅H₁₁·OH failed. 1 mol. of Br in AcOH containing a trace of HBr gives HBr and *bromosarsasapogenin acetate* (V), m.p. 195° (decomp.) or 208° (decomp.). Zn-Hg and conc. HCl in 95% EtOH reduce (I), (IV), or (V) [but not (II); R = CH₂·OH] to *tetrahydrosarsasapogenin* (VI), m.p. 193° [dibenzoate (VII), m.p. 149°; non-formation of a tribenzoate indicates steric hindrance at C₁₆], oxidised by CrO₃ to a mixture, which yields a *disemicarbazone*, C₂₉H₄₈O₄N₆, of an acid. CrO₃-AcOH oxidises (VII) to a product, hydrolysed to a substance, C₂₇H₄₆O₃, m.p. 143°. Br-AcOH does not attack (III). SeO₂



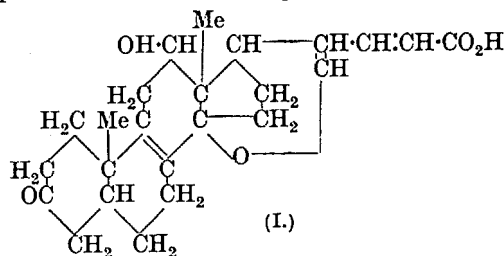
oxidises (I) in C₆H₆-AcOH, but the products could not be purified; [(II), R = CH₂·OH], (VI), bromosarsasapogenin, and (III) are unaffected by SeO₂. Conc. HCl in hot 95% EtOH isomerises (IV) to *isosarsasapogenin* (VIII), m.p. 185° (acetate, m.p. 152°; benzoate, m.p. 175°; Br-derivative acetate, m.p. 170°), oxidised by CrO₃ to *isosarsasapogenone* (IX), m.p. 188.5° (? = the ketone of Fieser *et al.*, A., 1938, II, 108). HCl-EtOH isomerises sarsasapogenone similarly to (IX). Zn-HCl-EtOH reduces (IX) to *deoxyisosarsasapogenin*, C₂₇H₄₄O₂, m.p. 140°, also obtained from deoxysarsasapogenin by HCl-EtOH. H₂-PtO₂ at 70°/3 atm. reduces (VIII) in AcOH to (II), (R = CH₂·OH), and Zn-Hg-HCl-EtOH gives (VI). SeO₂ oxidises (VIII) to a mixture. R. S. C.

Sterols. LVI. Sarsasapogenin derivatives. *epiSarsasapogenin*. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 943-944).—Reactions of sarsasapogenin (I) indicate a 3(β)-OH.

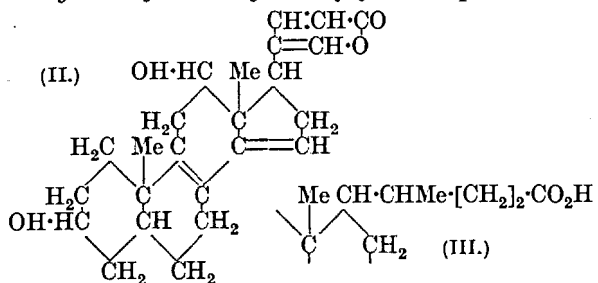
Its acetate and Na-*n*-C₅H₁₁·OH give *episarsasapogenin* (II), m.p. 207° [acetate, m.p. 194° (Br-derivative, m.p. 180°)], hydrogenated (PtO₂) in AcOH at 70°/3 atm. to *epidihydrosarsasapogenin*, m.p. 136°, but converted by Clemmensen reduction into oils. Sarsasapogenone with Al(OPrⁱ)₃-PrⁱOH at 100° gives a mixture of (I) and (II), and with H₂-PtO₂ in abs. EtOH at room temp./3 atm. yields (II). R. S. C.

Sterols. LVIII. Position of the nuclear hydroxyl groups in chlorogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 946-949).—The OH of chlorogenin (I) are proved to be in positions 3 and 6. In 80% EtOH (I) gives a digitonide and thus contains a 3(β)-OH. Chlorogenone (II) with KOH-EtOH gives a complex mixture, but it is unchanged by HCl-EtOH and thus probably has the *allo*-configuration at C₁₅; it is, moreover, only slightly epimerised by Na in *n*-C₅H₁₁·OH. Zn or Zn-Hg in HCl-EtOH reduces (II) to a compound, C₂₇H₄₄O₂, m.p. 177-178°; cholestan-7-one or cholestan-3:6-dione (III) gives similarly cholestan-7-one. (II) gives a *disemicarbazone*, darkens at 250°, m.p. >290°, and a *pyridazine*, decomp. ~270°, m.p. >290°. *o*-C₆H₄(NH₂)₂ and (III) give only a monocondensation product, C₃₃H₅₀ON₂, m.p. 207-210° (decomp.). R. S. C.

Toad venom. IX. Constitution of cinobufagin. J. KAWADA and M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 35, 419-425; cf. A., 1938, II, 416).—Cinobufagone and hot 5% KOH-MeOH yield *deacetylcinobufagonic acid* (I), m.p. 218-221°. Cinobufagin is dehydrated and

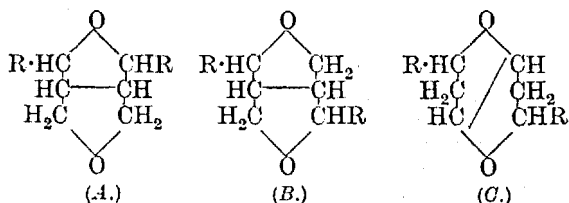


hydrolysed by hot HCl-EtOH to give *anhydrodeacetylcinobufagin* (II), m.p. 227-229°, which with Ac₂O-NaOAc at 100° gives only a *monoacetate*, m.p. 204-205°, and with H₂-Pd-black in AcOH yields *octahydroanhydrodeacetylcinobufagin*, m.p. 207.5-



208.5° (*monoacetate*, m.p. 207-209°, shows location of a sterically hindered OH at C₁₂), and *cinobufaginidihydroxycholanolic acid* (III), m.p. 144-147°. CrO₃-AcOH-H₂SO₄ oxidises (III) to the corresponding *diketo-acid*, m.p. 191-195°. R. S. C.

Constitution of asarinin. F. VON BRUCHHAUSEN and H. GERHARD (Ber., 1939, 72, [B], 830—838; cf. Kaku *et al.*, A., 1937, II, 259; Huang-Minlon, *ibid.*, 298).—Attempts are described to discriminate between the formulæ A, B, and C ($R = 3 : 4-(OH)_2C_6H_3$ ·

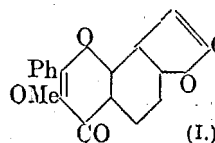


proposed for asarinin (I). Piperonyl chloride (improved prep. from the acid and $SOCl_2$) and $CH_3NaAc \cdot CO_2Et$ afford *Et piperonylacetoacetate*, which loses Ac when warmed with a NH_4Cl-NH_3 buffer giving *Et piperonylacetae*, m.p. 42.5°. This is transformed by successive treatments with NaOEt in EtOH-Et₂O and I in Et₂O into Et₂ αα'-dipiperonylsuccinate (II), m.p. 162° (accompanied by a non-cryst. form), readily converted by Ac₂O containing a little conc. H₂SO₄ at 100° into Et₂ 2 : 5-di-3' : 4'-methyleneedioxyphenylfuran-3 : 4-dicarboxylate, m.p. 118° [corresponding acid, m.p. 234°, and its anhydride, decomp. 277° (block)]. Attempts to hydrogenate the furan nucleus were fruitless. (II) is reduced by Al-Hg and EtOH to Et₂ di(hydroxy-3 : 4-methyleneedioxyphenylmethyl)succinate, ring-closure of which to Et₂ 2 : 5-di-3' : 4'-methyleneedioxyphenyltetrahydrofuran-3 : 4-dicarboxylate, m.p. 133—134°, takes place with very small yield so that synthetic methods are impossible. Hydrogenation (PtO₂ in AcOH) of (I) leads to the absorption of 8 H₂, of which 6 H₂ are required by the aromatic double linkings. With Pd-C only 2 H₂ are absorbed, giving a diol (III), C₂₀H₂₂O₆, m.p. 103—104°, which, contrary to Dieterle and Schwengler (A., 1939, II, 171) [who worked with xanthoxylin S, identical with (I)], is optically active, having $[\alpha]_D^{25} +29.8^\circ$ in CHCl₃. It does not yield AcOH when oxidised according to Kuhn and Orsa. The observations are incompatible with formula A. (III) is indifferent to the prolonged action of HIO₄; formula C is therefore impossible. Reduction of cubebin (IV) with Al-Hg in EtOH-Et₂O affords dihydrocubebin (V), m.p. 104°, $[\alpha]_D^{25} -30.6^\circ$, which is the optical antipode of (III). The corresponding r-compound has m.p. 90—93° after softening at 80°. Sesamin is reduced catalytically to (V). (I) has therefore the structure B, which can also be applied to eudesmin and pinosresinol if $R = C_6H_3(OMe)_2$ and $OH \cdot C_6H_3 \cdot OMe$ respectively. Dieterle's proposal to abolish the name asarinin in favour of xanthoxylin S is resisted. Contrary to Ishigaro (A., 1937, II, 33), reduction of (IV) does not occur with the customary amount of PtO₂ in AcOH; with an increased amount of catalyst the aromatic double linkings are involved.

H. W.

Synthetic experiments in the benzopyrone series. I. Synthesis of karanjin-α-carboxylic acid. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 259—264).—7-Hydroxy-3-methoxy-2-methylchromone-8-aldehyde is converted by NaOMe in anhyd. MeOH into the Na salt, transformed by $CH_2Br \cdot CO_2Et$ at 170—175° into the

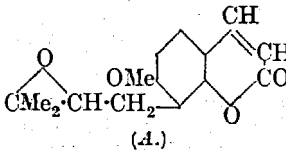
carbethoxymethyl ether, m.p. 180°. The method is not successful with 7-hydroxy-3-methoxyflavone-8-aldehyde, which, however, is converted by $CH_2Br \cdot CO_2Et$ in boiling C₆H₆ containing anhyd. K₂CO₃ into its carbethoxymethyl ether, m.p. 116—117°, which with boiling aq. 5% KOH suffers hydrolysis and simultaneous ring-closure to 3-methoxyflavono-7 : 8-furan-2-carboxylic acid (I), m.p. 224—226° (sparingly sol. Na salt), considered to be karangin-α-carboxylic acid. (I) is stable under conditions which usually involve decarboxylation and at a higher temp. undergoes a complex change. H. W.



Auraptin. H. BÖHME and G. PIETSCH (Ber., 1939, 72, [B], 773—779; cf. A., 1939, II, 32).—Auraptin (I), dissolved in an excess of MeOH-NaOMe, is transformed by alternate applications of NaOMe and Me₂SO₄ into cis-auraptenic acid (II), m.p. 150°, $[\alpha]_D^{25} +2^\circ$ in EtOH, also obtained by the prolonged action of NaOMe alone at room temp. Attempted methylation of (I) by MeI-NaOMe in boiling MeOH yields trans-auraptenic acid (III), m.p. 204°, $[\alpha]_D^{25} +90.4^\circ$ in EtOH, obtained without intervention of MeI. (III) is converted by CH_2N_2 into the Me ester, m.p. 99°, whereas a pure product could not be obtained analogously from (II). (II) and (III) are regarded as cis-trans-isomerides since (II) is transformed into (III) by NaOMe-MeOH at 100°, by irradiation in Et₂O, or when heated at its m.p. Further (II) and (III) are hydrogenated to dihydroauraptenic acid, m.p. 99—100°, identical with that obtained (*loc. cit.*) from (I). With NHPH-NH₂ in dil. AcOH (I) affords a product, m.p. 136°, but it is not possible to establish whether this is an additive compound or a phenylhydrazone. Boiling 20% H₂SO₄ isomerises (I) to isauraptin (IV), m.p. 66°, in which the presence of CO is established by the isolation of an oxime, m.p. 166—167°. The presence of an oxide O in (I) is confirmed by its transformation by boiling 1% H₂C₂O₄ into auraptin hydrate, C₁₅H₁₈O₆, m.p. 128—129°, $[\alpha]_D^{25} -43.8^\circ$ in EtOH, which contains 2 active H (Zerevitinov) and is transformed by 20% H₂SO₄ into (IV). NHMe₂ and (I) in C₆H₆ at 150° afford the substance, C₁₇H₂₃O₄N, m.p. 170°, $[\alpha]_D^{25} +78.8^\circ$ in EtOH.

H. W.

Oxidative degradation and constitution of auraptin. H. BÖHME and E. SCHNEIDER (Ber., 1939, 72, [B], 780—784).—Cryst. degradation products are not obtained by treating auraptin (I) with molten KOH or with O₃ but oxidation with CrO₃ in AcOH affords 7-methoxycoumarin-I-acetic acid (II), m.p. 254—255° (Me ester, m.p. 154—155°), identical with the product of the oxidation of osthol (III) (Späth and Pesta, A., 1933, 614) and COMe₂. (II) is decarboxylated to 7-methoxy-8-methylcoumarin, m.p. 136.5—137.5°. Auraptin hydrate is oxidised by Pb(OAc)₄ (mol. ratio 1 : 1) to COMe₂ and 7-methoxycoumarin-8-acetaldehyde, m.p. 160°, converted by Ag₂O into (II).



(III) is converted by α -CO₂H·C₆H₄·CO₂H in Et₂O into an optically inactive form of (I), transformed by boiling 20% H₂SO₄ into isaurapten. (I) is therefore A.

H. W.

Dicyclic sulphonium salts with sulphur as branching atom. II. Sulphur analogue of quinuclidine. V. PRELOG and D. KOHLBACH (Ber., 1939, 72, [B], 672—675).—Et α -dibromopentane- γ -acetate, b.p. 164°/0.4 mm., is converted by K₂S in EtOH into Et thiopentamethylene-4-acetate,

$S \begin{matrix} \text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2 \end{matrix} \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b.p. 137—143°/10 mm.

(free acid, m.p. 169—171°), reduced by Na and abs. EtOH to β -4-thiopentamethylene-ethyl alcohol, b.p. 145°/10 mm. This is converted by 68% HBr at 60° into the corresponding bromide, which at 100° passes into dicyclo[2 : 2 : 2]thianium-1-octane bromide (I), m.p. 280—281° (corresponding chloride, sublimes at 250°; platinichloride; picrate, decomp. ~305°). The free base is a pale yellow liquid.

H. W.

Sulphur analogues of furan types. A. L. JACOBY (Iowa State Coll. J. Sci., 1938, 13, 70—72).—Dibenzthiophen (I) with AcCl and AlCl₃-CS₂ affords 3-acetyldibenzthiophen, m.p. 111°, oxidised (NaOH-I) to dibenzthiophen-3-carboxylic acid (Me ester, m.p. 74—75°). (I) with LiBu^t followed by treatment with CO₂ affords dibenzthiophen-1-carboxylic acid (65%), m.p. 252—253° (Me ester, m.p. 95°). LiPh and 1-LiC₁₀H₇ give small yields; *p*-OMe·C₆H₄Li does not react. (I) with CaPhI as above gives dibenzthiophen-2(?) -carboxylic acid, m.p. 300—305° (decomp.) (Me ester, m.p. 129—130°), decarboxylated to (I). Fusion of (I) with Hg(OAc)₂ gives a monoacetoxymercuri-derivative, m.p. 215° (decomp.), together with some polymercurated material. Li 1-dibenzthienyl (II) with O₂ gives 1-hydroxydibenzthiophen (III), m.p. 167° (OMe-derivative, m.p. 123°), converted by warm conc. HNO₃-AcOH into a (NO₂)₂-derivative, m.p. 204° (decomp.). (III) with NaHSO₃-NH₃ (d 0.88) affords 1-aminodibenzthiophen, m.p. 110° (acetate, m.p. 198°, which with Br gives 4-bromo-1-acetaminodibenzthiophen, m.p. 254°), also obtained by heating 1-bromodibenzthiophen [prepared from (II) and Br] with NH₃ (d 0.88) and Cu₂Br₂ under pressure. 3-Acetamidodibenzthiophen, m.p. 178° (lit., 168°), with fuming HNO₃-Ac₂O affords (?) -nitro(?) -acetamidodibenzthiophen, m.p. 209° [hydrolysed (EtOH-HCl) to a N-free compound, m.p. 88°], and a small amount of (?) -nitro(?) -aminodibenzthiophen, m.p. 248—250° (decomp.). When Ph₂ is heated with S and AlCl₃, (I) is formed but the method cannot be used to synthesise derivatives of (I) because of the formation of polymerides. Succinic anhydride with (I) and AlCl₃ affords β -3-dibenzthiophenoylpropionic acid, m.p. 160.5 161°, reduced (Zn-HCl) to γ -3-dibenzthienylbutyric acid, m.p. 131°, which with H₂SO₄ affords 1-keto-1 : 2 : 3 : 4-tetrahydrothiobrazan, m.p. 178°. Similarly, (I) with α -C₆H₄(CO₂)₂O gives α -3-dibenzthiophenoylbenzoic acid [+H₂O (unstable), m.p. 120—125°; Et ester, m.p. 105—106°], cyclised by fusion with AlCl₃-NaCl to

thionaphthenoanthraquinone, m.p. 285—286°. (I) with Na in liquid NH₃ affords 1 : 4-dihydrodibenzthiophen (IV), m.p. 76° (picrate, m.p. 105°), which absorbs 2 Br; when warmed the bromide loses HBr and regenerates (I). (IV) with LiPh affords (I), C₆H₆, and LiH; the last two are derived from LiPh by reduction.

J. L. D.

Action of various reagents on trimethyleneimine. J. M. JANBIKOV (J. Gen. Chem. Russ., 1938, 8, 1470—1475).—(CH₂)₃NH gives NH₃, H₂O, and CH₂:CH·CHO with H₂O, NH₃·CH₂:CH·CH₂, and NH₂:CH:CHMe with Al₂O₃ at 360°, trimethyleneimine N-methiodide, m.p. 133°, with MeI, N-phenyl-N'-trimethylenecarbamide, m.p. 189—190°, with PhNCO, and a mixture of N-trimethyleneiminocarbinal and NN'-di(trimethyleneimino)methane, b.p. 67—69°/29 mm., with paraformaldehyde (I) at room temp.; at 110—115° (5 hr.) the product with (I) is 2-hydroxymethyltrimethyleneimine, b.p. 54—55°/85 mm.

R. T.

Synthesis of trimethyleneimine, and the products of the reaction between *p*-toluenesulphonamide and $\gamma\gamma$ -dibromopropane. J. M. JANBIKOV (J. Gen. Chem. Russ., 1938, 8, 1545—1548).—*p*-C₆H₄Me·SO₂·NH₂, CH₂(CH₂Br)₂, and aq.-alcoholic KOH (2 hr. at 100°) yield a mixture of *p*-toluenesulphonyltrimethyleneimide, *p*-C₆H₄Me·SO₂·NH·(CH₂)₃·OH, and *p*-C₆H₄Me·SO₂·N[(CH₂)₃·OH]₂.

R. T.

Catalytic transformations of heterocyclic compounds. X. Synthesis of certain N-substituted pyrroles, N- and α -substituted pyrrolidines, and α -methylthiophen. J. K. JURIEV (J. Gen. Chem. Russ., 1938, 8, 1934—1938).—2-Methyltetrahydrofuran (I) and NH₃ passed over Al₂O₃ at 400° yield 2-methylpyrrolidine; with H₂S in place of NH₃ the product is 2-methylthiophen. Furan or tetrahydrofuran and NH₂Me or NH₂Et similarly afford 1-methyl- or 1-ethyl-pyrrole or -pyrrolidine, whilst (I) and NH₂Me or NH₂Et give 1 : 2-dimethyl- or -diethyl-pyrrolidine.

R. T.

1-Azadicyclo[1 : 2 : 3]octane. V. PRELOG, (Miss) S. HEIMBACH, and E. CERKOVNIKOV (J.C.S., 1939, 677—678).—3- β -Bromoethylpiperidine hydrobromide, m.p. 116—116.5°, prepared from the corresponding OH-compound and HBr, with NaOH followed by PhSO₂Cl gives 1-azadicyclo[1 : 2 : 3]octane (hydrochloride, sublimes above 300°; platinichloride, m.p. 215—215.5°; picrate, m.p. 294—295°).

F. R. S.

Piperidine derivatives. XIV. Local anaesthetics derived from α -picoline. C. W. TULLOCK and S. M. McELVAIN (J. Amer. Chem. Soc., 1939, 61, 961—964; cf. A., 1934, 81).— β -3-Pyridylethyl alcohol (from α -picoline and paraformaldehyde at 135—140°/133 atm. in H₂), b.p. 107—108°/7 mm., with H₂-Raney Ni in dioxan at 150—160°/260 atm. gives β -2-piperidylethyl alcohol (I), b.p. 105—108°/7 mm., 223—226°/760 mm. Chloral and α -picoline at 112—113° give 2- $\gamma\gamma$ -trichloro- β -hydroxypropylpyridine (II), m.p. 85—86°, which by hydrolysis, loss of H₂O, and esterification yields Et β -2-pyridylacrylate (III), b.p. 142—145°/11 mm. H₂-Raney Ni at 60°/135 atm. then yields γ -2-pyridylpropyl alcohol, the propionate

of which with H_2 -Raney Ni at $200^\circ/200$ atm. gives 93% of 3-keto-octahydropyrrocoline, reduced by H_2 -Raney Ni at $250^\circ/250$ atm. to octahydropyrrocoline. Na-EtOH reduces (II) in PhMe to β -2-piperidylisopropyl alcohol (IV), *cryst.*, b.p. $112-115^\circ/11$ mm. [oxidised to 2-piperidylacetone (V)], and a product, b.p. $130.5-132^\circ/9$ mm. [oxidised to a product other than (V)]. Na-EtOH reduces (III) to γ -2-piperidyl-n-propyl alcohol (VI), b.p. $102-105^\circ/3$ mm. *N*-Alkyl derivatives (C_1-C_4) of (I), (IV), and (VI) were prepared by CH_2O-HCO_2H , 0.5 mol. of RI, or K_2CO_3 and an excess of RI; their benzoate hydrochlorides have considerable anaesthetic power, but are irritant. The following are described, figures in parentheses being the m.p. of the hydrochlorides: β -2-1-methyl- ($139-140^\circ$), -ethyl- ($148-150^\circ$), -n-propyl- ($118-120^\circ$), and -n-butyl-piperidylethyl benzoate, b.p. $147-152^\circ/0.5$ mm.; γ -2-1-methyl- ($135-137^\circ$), -ethyl- ($114-116^\circ$), -n-propyl- ($139-141^\circ$), and -n-butylpiperidyl-n-propyl benzoate ($132-134^\circ$); β -2-1-methyl-, b.p. $123-127^\circ/0.5$ mm., -ethyl-, b.p. $118-122^\circ/0.5$ mm., -n-propyl-, b.p. $139-141^\circ/0.5$ mm., and -n-butyl-piperidylisopropyl benzoate, b.p. $143-147^\circ/0.5$ mm. R. S. C.

Action of bromine on *N*-substituted 2-pyridones. J. A. GAUTIER (Compt. rend., 1939, 208, 816-818; cf. A., 1938, II, 68).—*N*- β -Hydroxyethyl-2-pyridone (I) (1 mol.) with 4 Br in AcOH affords 3:5-dibromo-*N*- β -hydroxyethyl-2-pyridone, m.p. 168.5° (benzoate, m.p. 107°), converted by PBr_5-PBr_3 at 150° (sealed tube) into 2:3:5-tribromopyridine. Similarly *N*-(β -hydroxy- β -phenylethyl)-2-pyridone (II) affords 3:5-dibromo-*N*-(β -hydroxy- β -phenylethyl)-2-pyridone, m.p. 166° , but *N*-substituted hydroxyalkoxy-2-pyridones are decomposed. (I) and (II) (1 mol.) with 2 Br in $CHCl_3$ give the corresponding hydrobromides and small amounts of highly brominated compounds. Bromination in H_2O gives non-isolable blue compounds destroyed by alkali.

J. L. D.

Vitamin- B_6 . A. ICHIBA and K. MICHl (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1938, 35, 73-77).—Vitamin- B_6 , $[\alpha]_D^{25} -0.9^\circ$ in EtOH, yields Ac_3 , b.p. $145-150^\circ/0.17$ mm., Bz_3 (from the hydrochloride and $BzCl$ in C_5H_5N), m.p. $121-122^\circ$, and *N*-Me and *O*-Me derivatives (from the hydrochloride and CH_2N_2 in MeOH), m.p. $190-193^\circ$ and $103-105^\circ$, respectively. The vitamin hydrochloride, distilled with Zn dust, gives a substance with an odour of C_5H_5N . The *O*-Me derivative is oxidised ($KOH-KMnO_4$) to a neutral substance, $C_9H_9O_3N$, m.p. $105-107^\circ$, and an acid, $C_7H_7ON(CO_2H)_2$, m.p. $217-219^\circ$ (decomp.) (*Ba* salt). The vitamin may be a substituted hydroxypyridine. A. LI.

Vitamin- B_6 . A. ICHIBA and K. MICHl (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 36, 1-5; cf. A., 1938, III, 1026).—*N*-Methyladermin (from adermin and CH_2N_2) is oxidised by $KMnO_4-KOH$ to *N*-methyloxamic acid. The Me 3-methoxy-pyridinedicarboxylate formed by partial oxidation of adermin Me ether (Kuhn *et al.*, A., 1939, II, 177) on heating yields substances, $C_8H_9O_3N$, m.p. $228-230^\circ$, and $C_8H_{11}O_4N$, m.p. 200° . J. D. R.

Reaction of ethylene oxides with pyridine derivatives. H. LOHMANN (J. pr. Chem., 1939,

[ii], 153, 57-64).— C_5H_5N or quinoline derivatives (1 mol.) with $\alpha\beta$ -oxides (1 mol.), alone or in solvents (best MeOH), at room temp. or 60° give yellow, red, or brown substances (probably mixtures), which are not 1:1 additive compounds and are dyes. Me favours, NH_2 or CO_2H hinders, the reaction, which is sp. Piperidine reacts readily. R. S. C.

Mixed platinum dichlorodiammines possessing a *cis*-configuration.—See A., 1939, I, 334.

Direct synthesis of 3:5-di-iodopyridine. P. BAUMGARTEN (Ber., 1939, 72, [B], 859).—The yield of 3:5-di-iodopyridine from $ONa\cdot CH_3\cdot CH\cdot CH\cdot CH\cdot CH\cdot N\cdot SO_3Na$ and I can be nearly trebled (cf. A., 1939, II, 226) if KOAc is added to the mixture to react with the liberated acid. H. W.

Aromatic nitro-derivatives. XVII. Reactivity of 2-chloro-5-nitropyridine. XVIII. Substituted nitropyridines. A. MANGINI and B. FRENGUELLI (Gazzetta, 1939, 69, 86-96, 97-104).—XVII. 2-Chloro-5-nitropyridine (I) is compared with 4:1:3- $C_6H_3Cl(NO_2)_2$ (II) for reactivity with p - $C_6H_4Br\cdot NH_2$, p - $C_6H_4Ph\cdot NH_2$, NH_2Ph , p - $C_6H_4Me\cdot NH_2$, N_2H_4 , H_2O , and piperidine; after 20 or 40 min. at 35° or 45° , the mixture is treated with dil. $AgNO_3-HNO_3$ and residual $AgNO_3$ titrated. Reactivity with NaOMe and NaOEt is also studied. Results (tabulated) show that Cl in (I) has a reactivity similar to but smaller than that of Cl in (II). Thus NO_2 has a greater activating effect than presence of heterocyclic N in a similar position. The results are discussed in relation to Bonino's structural theories. The relation between constitution and reactivity of other C_5H_5N and quinoline derivatives is also discussed.

XVIII. The following are prepared from 2-chloro-5-nitropyridine (I) and p - $C_6H_4R\cdot NH_2$: 5-nitro-2-p-toluidino-, m.p. $137-138^\circ$; -2-p-diphenylamino-, m.p. $199-200^\circ$; and -2-p-hydroxy-, m.p. $211-212^\circ$, -2-p-methoxy-, m.p. $160-161^\circ$, -2-p-ethoxy-, m.p. $140-141^\circ$, -2-p-NN-dimethylamino-, m.p. $186-187^\circ$, and -2-p-bromo-anilino-pyridine, m.p. $154-155^\circ$. Using piperidine and N_2H_4 , 5-nitro-2-piperidino-, m.p. $83.5-84.5^\circ$, and -2-hydrazino-pyridine, m.p. $205-206^\circ$ (decomp.) (*Ac* derivative, m.p. $175-176^\circ$), are respectively obtained. The last with PhNCS gives γ -phenyl- α -5-nitro-2-pyridylisothiosemicarbazide, $NHPh\cdot C(SH)\cdot N\cdot NH\cdot C_5H_4N\cdot NO_2$ (III), which from EtOH is obtained in the stable *trans*-form (*A*), m.p. $182-183^\circ$, and from conc. HCl in the labile *cis*-form



(B), m.p. $155-160^\circ$. With PhCHO, (III) gives a compound, $CHPh[S\cdot C(NHPh)\cdot N\cdot NHR]_2$, m.p. $239-240^\circ$ (decomp.). E. W. W.

Theory of hydrolysis of amines. Hydrolysis of nitroso- and nitro-derivatives of 2:6-diamino- and 2-amino-6-hydroxy-pyridine. A. I. TIROV (J. Gen. Chem. Russ., 1938, 8, 1483-1491).—2-Amino-6-hydroxypyridine and $NaNO_2$ in AcOH yield 3-nitroso-2-amino-6-hydroxypyridine; this, or 3-nitroso-2:6-diaminopyridine, and 8% HCl at room temp. give 3-nitroso-2:6-dihydroxypyridine. 3-Nitro-2-amino-6-hydroxy- or 3-nitro-2:6-diamino-pyri-

dine are similarly hydrolysed to 3-nitro-2:6-dihydroxypyridine. R. T.

2-Aminopyridine-5-sulphonic acid and derivatives. A. E. TSCHITSCHIBABIN and M. VIALATOUT (Bull. Soc. chim., 1939, [v], 6, 736—739; cf. A., 1939, II, 35).—2-Aminopyridine and 20% oleum at 140—145° give the 5-sulphonic acid. 2-Chloropyridine-5-sulphonyl chloride and 2-aminopyridine give 2-chloropyridine-5-sulphon-2'-pyridylamide, converted by NH_3 (+NaI) at 180—190° into the 2- NH_2 -analogue, m.p. $\sim 195^\circ$. Similarly prepared are 2-chloro- and 2-amino-pyridine-5-sulphonbenzylamide, m.p. 142°. A. T. P.

Catalytic hydrogenation of mixtures of hydrochloides of pyridine bases. M. I. USCHAKOV, M. I. IVANOVA, and N. F. KOSCHELEVA (J. Gen. Chem. Russ., 1938, 8, 1870—1872).— $\text{C}_5\text{H}_5\text{N}$ is hydrogenated (Pt-black) before the second component of the systems $\text{C}_5\text{H}_5\text{N}$ - α -, β -, and γ -picoline, $\alpha\alpha'$ -lutidine, and α -quinoline, and α -picoline- $\alpha\alpha'$ -lutidine (all as hydrochloides, in EtOH), and α -picoline is hydrogenated before lutidine. Selective hydrogenation in binary systems of isomeric picolines is not observed. R. T.

Synthesis of dibenzopyridocoline derivatives. II. Syntheses of 4':5'-dimethoxy-4''':5''-methylenedioxy-3:4:5:6-tetrahydro-(1':2':1:2:1'':2'':7:8-dibenzopyridocoline) and the corresponding tetramethoxy-derivative. S. SUGASAWA and K. KAKEMI (Proc. Imp. Acad. Tokyo, 1939, 15, 52—55).—6:7-Dimethoxy-N-(β -3':4'-methylenedioxyphenylethyl)-3:4-dihydroisoquinolinium bromide (+0.5 H_2O), m.p. 187—188°, is oxidised [C_6H_6 -alkaline $\text{K}_3\text{Fe}(\text{CN})_6$] and cyclised to 4':5'-dimethoxy-4''':5''-methylenedioxy-3:4:5:6-tetrahydro-9:10-dehydro-(1':2':1:2:1'':2'':7:8-dibenzopyridocolinium iodide) (+0.5 H_2O), m.p. 188—189° [chloride (+1.5 H_2O), m.p. 150°]; this chloride is reduced catalytically to 4':5'-dimethoxy-4''':5''-methylenedioxy-3:4:5:6-tetrahydro-(1':2':1:2:1'':2'':7:8-dibenzopyridocoline) (+0.5 H_2O), m.p. 101—102° [hydriodide, m.p. 209° (decomp.)]. A similar series of reactions gives 6:7-dimethoxy-N-(β -3':4'-dimethoxyphenylethyl)-3:4-dihydroisoquinolinium bromide, m.p. 192°; 4':5':4'':5''-tetramethoxy-3:4:5:6-tetrahydro-9:10-dehydro-(1':2':1:2:1'':2'':7:8-dibenzopyridocolinium iodide) (+0.5 H_2O), m.p. 195°; and 4':5':4'':5''-tetramethoxy-3:4:5:6-tetrahydro-(1':2':1:2:1'':2'':7:8-dibenzopyridocoline), m.p. 116°. F. R. S.

Destructive hydrogenation of quinoline. I. I. ERU, E. M. SACHNOVSKAJA, and V. A. PRITSCHKO (J. Gen. Chem. Russ., 1938, 8, 1563—1575).—The chief product of hydrogenation of quinoline at 200°/135 atm. is 1:2:3:4-tetrahydroquinoline, which at 400—500° (initial H_2 pressure 100 atm.) in presence of MoS_3 catalyst gives a mixture of methyl- and ethyl-cyclopentane, cyclohexane, methyl- and ethyl-cyclohexane, PhEt , PhPr^a , dihydrocarbazole, methyl- and ethyl-cyclohexylamine, methyl- and ethyl-di- and -tetra-hydroaniline, NHPHPr^a , 2:3-dihydro-indole and -skatole, hexahydroquinoline, and a no. of unidentified products. R. T.

Oxidation of some β -phenylethyl-pyridinium and -quinolinium salts. S. SUGASAWA and N. SUGIMOTO (Proc. Imp. Acad. Tokyo, 1939, 15, 49—51).—Oxidation [alkaline $\text{K}_3\text{Fe}(\text{CN})_6$] of β -phenylethyl-pyridinium and -quinolinium salts with a free p -position to OMe gives only resinous products but without a free p -position or no OMe, the corresponding pyridone and quinolone derivatives are obtained. The following are described: N- β -3':4'-methylenedioxyphenyl-2-pyridone (I), m.p. 148°; N- β -4'-methoxyphenylethyl-2-quinolone, m.p. 110.5°; and N- β -3':4'-methylenedioxyphenylethyl-2-quinolone (II), m.p. 138°. Cyclisation (POCl_3) of (I) affords 4':5'-methylenedioxy-9:10-dehydro-3:4-dihydro-(1':2':1:2-benzopyridocolinium chloride), m.p. 191°, hydrogenated to the corresponding hydro-pyridocoline base (hydrochloride, m.p. 213°); similarly (II) gives 4':5'-methylenedioxy-9:10-dehydro-3:4-dihydro-(1':2':1:2:1'':2'':5:6-dibenzopyridocolinium chloride), m.p. 254° (decomp.), forming a hydrobase (hydrochloride, m.p. about 227°). F. R. S.

Behaviour of 8-hydroxyquinoline with diazomethane. G. CARONNA and (SIGNA.) B. SANSONE (Gazzetta, 1939, 69, 24—28).—8-Hydroxyquinoline and CH_2N_2 in Et_2O give 8-keto-5:6-methylene-5:6:7:8-tetrahydroquinoline (?), m.p. 115° (decomp.) [platnichloride, m.p. 240° (decomp.)], with some 8-methoxyquinoline. E. W. W.

Synthesis of nitrogen ring compounds. XVII. Synthesis of some 1:2-polymethylenetetrahydroisoquinolines. S. SUGASAWA, K. SAKURAI, and N. SUGIMOTO (Proc. Imp. Acad. Tokyo, 1939, 15, 82—85).—Interaction of 3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ (I) and succinic anhydride (II) in C_6H_6 yields N- β -(3:4-dimethoxyphenyl)ethylsuccinamic acid, m.p. 108.5°, converted by Ac_2O - $\text{C}_5\text{H}_5\text{N}$ into the succinimide, m.p. 130° (lit. 129°), which on electrolytic reduction in AcOH - H_2SO_4 , followed by treatment with POCl_3 in PhMe , yields 6:7-dimethoxy-1:2-trimethylene-3:4-dihydroisoquinolinium chloride [picrate, m.p. 193—194° (decomp.) (lit. 200—201°)], which on catalytic reduction gives the 1:2:3:4- H_4 -compound, m.p. 87—88° (lit. 88—89°) [picrate, m.p. 186° (lit. 187°)]. By the same methods, from (II) and β -piperonyl- α -methyl-ethylamine (III) are formed successively N- α -methyl- β -(3:4-methylenedioxyphenyl)ethylsuccinamic acid, m.p. 134.5°, N- α -methyl- β -(3:4-methylenedioxyphenyl)ethylsuccinimide, m.p. 80°, 6:7-methylenedioxy-1:2-trimethylene-3-methyl-3:4-dihydroisoquinolinium iodide, m.p. 245° (decomp.), and 6:7-methylenedioxy-1:2-trimethylene-3-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 75.5° [hydrochloride, m.p. 234° (decomp.)]. Similarly from (I) and glutaric anhydride (IV) are formed N- β -(3:4-dimethoxyphenyl)ethylglutarimide, m.p. 113—114°, 6:7-dimethoxy-1:2-tetramethylene-3:4-dihydroisoquinolinium picrate, m.p. 179—180° (lit. 185—186°), and 6:7-dimethoxy-1:2-tetramethylene-1:2:3:4-tetrahydroisoquinoline, an oil (lit. m.p. 59—60°) (perchlorate, m.p. 185°). From (III) and (IV) are formed N- α -methyl- β -(3:4-methylenedioxyphenyl)ethylglutaric acid, m.p. 95.5°, and 6:7-methylenedioxy-1:2-tetramethylene-3-methyl-1:2:3:4-tetrahydroisoquinoline, an oil (perchlorate,

m.p. 183—183.5°). From β -piperonylethylamine and adipic anhydride (V) is formed 6:7-methylenedioxy-1:2-pentamethylene-1:2:3:4-tetrahydroisoquinoline, an oil [picrate, m.p. 154° (decomp.)], and from (III) and (V), 6:7-methylenedioxy-1:2-pentamethylene-3-methyl-3:4-dihydroisoquinolinium iodide, m.p. 238—239° (decomp.). J. D. R.

Nitration of derivatives of 4-hydroxyquin-aldine. W. O. KERMACK and (MISS) A. P. WEATHERHEAD (J.C.S., 1939, 563—566).—Nitration of 4-hydroxy-2-methylquinoline gives the 6- NO_2 -derivative, m.p. above 400°, reduced (SnCl_2) to the 6- NH_2 -compound, m.p. 345° [Ac derivative (I), m.p. 365°]. 4-Hydroxy-2:3-dimethylquinoline is similarly nitrated to the 6- NO_2 -compound, m.p. 380°, reduced to the 6- NH_2 -derivative (II), m.p. 326°. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ give Et β -p-chloro-anilinoacronate, cyclised to 6-chloro-4-hydroxy-2-methylquinoline, m.p. 320—322°; Et β -p-bromo-anilinoacronate, m.p. 54°, is similarly converted into 6-bromo-4-hydroxy-2-methylquinoline, m.p. 338°. Et β -p-acetamidoanilinoacronate, m.p. 180°, is cyclised to (I), and Et β -p-acetamidoanilino- α -methylcrotonate, m.p. 169°, prepared from $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ and Et methylacetoacetate, similarly forms 6-acetamido-4-hydroxy-2:3-dimethylquinoline, m.p. 385°, hydrolysed to (II). 6-Nitro-4-hydroxy-2-methylquinoline and $\text{POCl}_3\text{-PCl}_5$ give 4-chloro-6-nitro-2-methylquinoline, m.p. 142°, which with $\text{C}_5\text{H}_{11}\text{N}$ yields the 4-piperidino-compound, m.p. 145°, and with $\text{NET}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ affords the 4- β -diethylaminoethylamino-derivative, m.p. 100—102°. The following are similarly prepared: 4-chloro-6-bromo-, m.p. 75°, -6-acetamido-, m.p. 210°, and -6-amino-, m.p. 145°, and 6-acetamido-4-piperidino-2-methylquinoline (+ H_2O), m.p. 87°; and 4- β -diethylaminoethylamino-6-acetamido-2-methylquinoline hydrochloride, m.p. 272°. F. R. S.

Acridones. XII (1). Direct halogenation of substances of the acridone type. I. TANASESCU and E. RAMONTIANU (Bull. Soc. chim., 1939, [v], 6, 486—491).—With Br in AcOH, acridone yields 2:3-dibromoacridone, m.p. >360°, whilst 5-hydroxy-(I), 2-chloro-5-hydroxy-, and 3-nitro-5-hydroxy-acridone 10-oxides yield respectively 2:3-dibromo-, m.p. >360° (Bz derivative, m.p. ~172°), 2-chloro-3-bromo-, m.p. >360°, and 2-bromo-3-nitro-5-hydroxy-acridone 10-oxide, m.p. >360°. With Cl_2 in AcOH, acridone yields a mixture of Cl-compounds (containing $>\text{Cl}_4$), whilst (I) yields a 2:3- Cl_2 -derivative, m.p. >360° (Bz derivative, m.p. ~167°) (converted by boiling the PhNO_2 solution into 2:3-dichloroacridone), and a tetrachloroacridone, m.p. >360°. A. Li.

Acridine derivatives as antimalarials. II. U. P. BASU and S. J. DAS-GUPTA (J. Indian Chem. Soc., 1939, 16, 100—106; cf. A., 1938, II, 340).— $\text{o-C}_6\text{H}_4\text{MeCl}$ and ClSO_3H , first at 0° and then at 60°, give a product, converted by aq. NH_3 into 2-chloro-4-sulphonamidotoluene, m.p. 121—123°, which is oxidised by hot 10% KMnO_4 to 2-chloro-4-sulphonamido-benzoic acid (I), m.p. 198—199°. With $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, K_2CO_3 , and a little Cu powder in hot $\text{C}_5\text{H}_{11}\cdot\text{OH}$ (I) gives 5-sulphonamido-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 242°, converted

by hot POCl_3 into 5-chloro-2-sulphonamido-7-methoxy-acridine, decomp. >240°, which with $\text{NET}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{NH}_2$ or $\text{NET}_2\cdot[\text{CH}_2]_4\cdot\text{NH}_2$ in PhOH gives 2-sulphonamido-7-methoxy-5- β -diethylamino- α -methyl-n-butyl-, m.p. 115—120°, and -5- β -diethylamino-n-butyl-aminoacridine, m.p. 110—115°, respectively. $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ and ClSO_3H , first at 0° and then at 90—95°, give 4-chloro-2-carboxybenzenesulphonyl chloride, m.p. 101°, converted by aq. NH_3 or the appropriate amine into 2-chloro-5-sulphonamido-, m.p. 217—219°, 2-chloro-5-sulphondithylamido-, m.p. 147°, and 2-chloro-5-sulphonanilido-benzoic acid, m.p. 194—195°. With $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ etc. these give 4-sulphonamido-, m.p. 239—240°, 4-sulphondithylamido-, m.p. 170—171°, and 4-sulphonanilido-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 233°, and thence by POCl_3 5-chloro-3-sulphonamido-, decomp. >230°, -3-sulphondithylamido-, m.p. 184—186°, and -3-sulphonanilido-, m.p. 207—208°, -7-methoxyacridine. Condensation with the appropriate base in PhOH then yields 3-sulphonamido-, m.p. ~135°, 3-sulphondithylamido-, m.p. 240—241°, 3-sulphonanilido-7-methoxy-5- β -diethylamino- α -methyl-n-butylaminoacridine, m.p. ~105—110°, and 3-sulphonamido-, m.p. ~138°, 3-sulphondithylamido-, m.p. 251—252°, and 3-sulphonanilido-5- β -diethylamino-n-butylaminoacridine, m.p. ~100—105°. $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ does not condense with $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$, but 2:4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$ gives 5-chloro-4'-sulphonamidodiphenylamine-2-carboxylic acid, m.p. 207°, which, however, is not converted into an acridine derivative by POCl_3 or $\text{POCl}_3\text{-PCl}_5$. 5-Chloro-4'-acetamidodiphenylamine-2-carboxylic acid (similarly prepared), m.p. 287—288°, and POCl_3 give 2:5-dichloro-7-acetamidoacridine, m.p. 242—243°, hydrolysed by hot 24% HCl to 2:5-dichloro-7-aminoacridine, decomp. >250°. R. S. C.

meso-Derivatives of acridine. XI. Preparation of acridone and certain of its derivatives, and of 5-chloroacridine. N. S. DROZDOV (J. Gen. Chem. Russ., 1938, 5, 1505—1511).—Diphenylamine-2-carboxylic acid in xylene and P_2O_5 , heated at the b.p. for 6 hr., give acridone in 57% yield. 4-Dimethylaminodiphenylamine-2-carboxylic acid and POCl_3 in xylene (4 hr. at the b.p.) similarly yield 3-dimethylaminoacridone; with excess of POCl_3 the product is 5-chloro-3-dimethylaminoacridone, m.p. 158—159°, which at 100° for 20 min. with PhOH gives 3-dimethylamino-5-phenoxyacridone, m.p. 180—181°. 2:4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{H}$, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, K_2CO_3 , and $\text{Cu}(\text{OAc})_2$, heated in $\text{C}_5\text{H}_{11}\cdot\text{OH}$ (2 hr. at the b.p.), yield 5-chloro-4'-dimethylaminodiphenylamine-2-carboxylic acid, m.p. 230—231° (decomp.), which with P_2O_5 , POCl_3 , or H_2SO_4 gives 8-chloro-2-dimethylaminoacridone, not melting at 300°; 5:8-dichloro-, m.p. 200—202°, and 8-chloro-5-phenoxy-2-dimethylaminoacridone, m.p. 163—164°, are prepared as above. Diphenylamine-2:2'-dicarboxylic acid and POCl_3 in xylene yield acridone-1-carboxylic acid, not melting at 300°. R. T.

Acridine. XX. Organo-metallic syntheses in the acridine series. K. LEHMSTEDT and F. DOSTAL (Ber., 1939, 72, [B], 804—806).—The action of MgPhBr on acridone (I) suspended in Et_2O gives

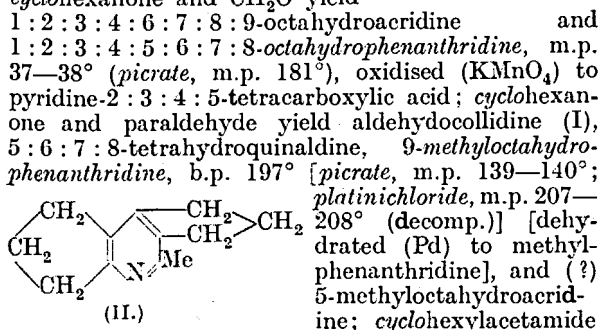
5-phenylacridine (II), m.p. 176°, in 19% yield. With LiPh and (I) in $C_6H_6-Et_2O$ the yield of (II) is 92%. Similarly 2-methylacridone and LiPh afford 9-phenyl-3-methylacridine, m.p. 114–115° (hydrochloride; additive compound with $HgCl_2$). 5-Cyanoacridine and LiPh in $C_6H_6-Et_2O$ give 5-benzoylacridine (III), m.p. 217–5°, 5-phenylacridylimino-methane, m.p. 243°, being obtained intermediately. Oxidation of 5-benzylacridine by $Na_2Cr_2O_7$ in boiling AcOH affords (III). H. W.

Pyrrole-indole group. Series II. XXIV. Mechanism of transformation of the pyrrole into the pyridine ring. B. ODDO. XXV. Syntheses by means of magnesylindoles. Tryptophol and 2-methyltryptophol. B. ODDO and (SIGNA.) F. CAMBIERI (Gazzetta, 1939, 69, 10–14, 19–24).—XXIV. This transformation probably proceeds by way of 1- and then 2-dichloromethylpyrrole. Reasons are adduced in support of this view, and against 3-substitution. The “3-nitro-2-methylpyrrole” of m.p. 111° is regarded as 5-nitro-2-methylpyrrole.

XXV. Mg indolyl bromide with $(CH_2)_2O$ in anhyd. C_6H_6 gives a product, regarded as the oxonium compound, $C_8H_6N^+O(MgBr) < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}$, which with H_2O followed by CO_2 gives tryptophol [compound with 1:2:4:6- $C_6H_2Me(NO_2)_3$, m.p. 72.5°] (cf. Hoshino *et al.*, A., 1935, 1379, who failed to effect the synthesis). Similarly Mg 2-methylindolyl bromide gives 2-methyltryptophol [β -(2-methyl-3-indolyl)ethyl alcohol], m.p. 56.5°, b.p. 202–204°/20 mm. [compound with 1:2:4:6- $C_6H_2Me(NO_2)_3$, m.p. 91–92°].

E. W. W.

Condensation of aldehydes and ketones with ammonia to give pyridine bases. Condensation with cyclic ketones. A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1939, [v], 6, 522–533).—With NH_4OAc and conc. aq. NH_3 at 180–200° under pressure, cyclohexanone and CH_2O yield



is formed in both cases. cyclopentanone, paraldehyde, and NH_4OAc yield (I) and a base $C_{12}H_{15}N$ (?) (II), b.p. 275° (corr.) (picrate, m.p. 134°; platinichloride).

A. Li.

Syntheses of hetero rings containing nitrogen. XIV. Synthesis of partly hydrogenated phenanthridine derivatives. I. S. SUGASAWA and K. KODAMA (Ber., 1939, 72, [B], 675–678).— ω -Nitro-2:4-dimethoxystyrene and dimethylbutadiene (I) in xylene at 175–180° give 5-nitro-4:3':4'-dimethoxyphenyl-1:2-dimethyl- Δ^1 -cyclohexene, m.p. 129–130°, electrolytically reduced in AcOH-HCl at a

R (A., II.)

Pb cathode to 5-amino-4:3':4'-dimethoxyphenyl-1:2-dimethyl- Δ^1 -cyclohexene (hydrochloride, decomp. 220°). The Bz derivative, m.p. 136–138°, is converted by $POCl_3$ in boiling xylene into 6:7-dimethoxy-9-phenyl-2:3-dimethyl-1:4:11:12-tetrahydrophenanthridine hydrochloride [m.p. 240–241° (decomp.)] (free base, m.p. 170–180°). Analogously, ω -nitro-3:4-methylenedioxy-styrene and (I) give 5-nitro-4:3':4'-methylenedioxyphenyl-1:2-dimethyl- Δ^1 -cyclohexene, m.p. 91°, converted through the non-cryst. amine and its formyl derivative into 6:7-methylenedioxy-2:3-dimethyl-1:4:11:12-tetrahydrophenanthridine, m.p. 157–158.5° [hydrochloride, m.p. 239° (decomp.)]. H. W.

Organic catalysts. XX. Synthetic carboxylases. VI. W. LANGENBECK and K. WEISSENBORN (Ber., 1938, 72, [B], 724–727; cf. A., 1938, II, 357).—The oximes of 1- and 4-ketotetrahydrophenanthrene respectively are transformed by HCl in AcOH- Ac_2O at 40° into 1- (I) and 4- (II), m.p. 55°, -amino-phenanthrene. (I) and $(OH)_2C(CO_2Et)_2$ at 100° yield Et 6:7-benzo- α -naphthdioxindole-3-carboxylate, which decomposes gradually when heated and is transformed by 30% NaOH at 100° into 6:7-benzo- α -naphthisatin; the oxime is reduced by $SnCl_2$ and conc. HCl in AcOH to 3-amino-6:7-benzo- α -naphthoxindole hydrochloride, the carboxylase activity of which somewhat exceeds that of 3-amino-6-methyl- α -naphthoxindole (III). (II) is similarly condensed to Et 8:9-benzo- α -naphthoxindole-3-carboxylate, whence successively 8:9-benzo-2-naphthisatin, its oxime, and 3-amino-8:9-benzo- α -naphthoxindole hydrochloride, which is catalytically less active than (III). H. W.

5:6-Benzoquinoline derivatives. J. BÜHM (Rocz. Chem., 1938, 18, 389–395).—2:5-, 2:6-, 2:7-, or 2:8- $NH_2 \cdot C_{10}H_6 \cdot SO_3H$, glycerol, conc. H_2SO_4 , and $PhNO_2$ heated at 150–160° for 8 hr. yield 5:6-benzoquinoline-3', m.p. 375–376° (decomp.), -4', decomp. 475°, -5', decomp. >420°, and -6'-sulphonic acid, m.p. 355–356° (decomp.). These acids, melted with KOH at 250–305°, yield 3', m.p. 245–247° (lit. 208–211°) (benzoate, m.p. 155.5–156°), 4', m.p. 289–292° (decomp.) (benzoate m.p. 163–164°), 5', m.p. 270–272° (decomp.) (benzoate, m.p. 144–145°), and 6'-hydroxy-5:6-benzoquinoline, m.p. 281–285° (decomp.) (benzoate, m.p. 114.5–115.5°). R. T.

2-Methyl-7:8-benzoquinoline-4-carboxylic acid. A. SILBERG (Bull. Soc. chim., 1939, [v], 6, 510–518).— α - $C_{10}H_7 \cdot NH_2$ with $AcCO_2H$ in EtOH yields 2-methyl-7:8-benzoquinoline-4-carboxylic acid (I) (A., 1936, 1520), m.p. 228–235° [NH_4 salt; Et ester (two forms), m.p. 85–87° and 88–90°]. (I) with $SOCl_2$ at 110° in sealed tubes yields the chloride, m.p. 162–164°, of 2-trichloromethyl-7:8-benzoquinoline-4-carboxylic acid, m.p. 240° (Et ester, m.p. 145°), the amide, m.p. 202° (from the chloride, together with a substance, m.p. 300°), of which with boiling aq. EtOH-NaOH gives 7:8-benzoquinoline-2:4-dicarboxylic acid (A., 1890, 1008) (Et₂ ester, m.p. 100–102°). The Ba or Ag salt of (I) when heated yields 2-methyl-7:8-benzoquinoline [picrate (mixture of two forms), m.p. 186–187°]. A. Li.

Pyrazolones.—See B., 1939, 551.

Substituted glyoxalines.—See B., 1939, 467.

Stereochemistry of quadricovalent atoms : gold.—See A., 1939, I, 244.

Aspartylhistidine. J. P. GREENSTEIN and F. W. KLEMPERER (J. Biol. Chem., 1939, 128, 245–250).—*N*-Carbobenzoyloxy-*L*-aspartic anhydride with *D*-histidine Me ester in CHCl_3 yields the Me ester, m.p. 95–105° (decomp.), of carbobenzoyloxy-*L*-aspartyl-*D*-histidine, m.p. 171° (decomp.), reduced (Pd in AcOH) to α -aspartylhistidine, m.p. 210°, $[\alpha]_D^{25}$ –6.0° in H_2O . The apparent dissociation consts. of this and of the β -isomeride (A., 1938, II, 459) have been measured by electrometric titration, and are discussed.

A. LI.

Substituted vinylbarbituric acids. III. Derivatives containing a dialkylvinyl group having five or more carbon atoms. A. C. COPE and (Miss) E. M. HANCOCK (J. Amer. Chem. Soc., 1939, 61, 776–779).— $\text{CHR}:\text{CR}':\text{CR}''(\text{CN})\cdot\text{CO}_2\text{Et}$, $\text{CO}(\text{NH}_2)_2$, and NaOEt give NH-compounds, hydrolysed to the barbituric acids, but, particularly if $\text{R}'' = \text{Pr}^i$, much alcoholysis to Et_3CO_3 and $\text{CHR}:\text{CR}'\text{CHR}''\text{CN}$ ($\rightleftharpoons \text{CH}_2\text{R}:\text{CR}'\text{CR}''\text{CN}$) occurs. The latter reaction is often minimised by using NaOPr^i instead of NaOEt or guanidine instead of $\text{CO}(\text{NH}_2)_2$. The acids, particularly those in which $\text{R} = \text{Et}$ and $\text{R}' = \text{Me}$, or $\text{R} = \text{Me}$ and $\text{R}' = \text{Et}$, are effective hypnotics, with high therapeutic ratios. The following are described. 5-Methyl-, m.p. 160–161°, 5-ethyl (I), m.p. 162–163°, 5-n- (II), m.p. 129.5–130.5°, and 5-iso-propyl-, m.p. 120–120.5°, 1:5-dimethyl-, m.p. 75–76°, and 1-methyl-5-ethyl-, m.p. 53–55°, 5- α -methyl- Δ^4 -butenylbarbituric acid, 5-Methyl-, m.p. 188.5–189.5°, 5-ethyl-, m.p. 174.5–175.5°, 5-n-, m.p. 152.5–153.5°, and 5-iso-propyl-, m.p. 125–126°, and 1-methyl-5-n-propyl-, m.p. 75–76°, 5- α -ethylpropenylbarbituric acid, 5-Methyl-, m.p. 161.5–162.5°, and 5-ethyl-5- α -methyl- Δ^4 -pentenylbarbituric acid (III), m.p. 127–128°. 5-Methyl-, m.p. 195–196°, and 5-ethyl- α -dimethyl- Δ^4 -butenylbarbituric acid, m.p. 188–188.5°. 5-Methyl-, m.p. 159.5–160°, and 5-ethyl-5- α -methyl- Δ^4 -hexenylbarbituric acid, m.p. 113.5–114°. 5-Ethyl-5- α -n-propyl- Δ^4 -butenylbarbituric acid, m.p. 138–139°. Structures are proved by ozonisation of (I), (II), and (III) to the appropriate aldehydes; traces of CH_2O formed are derived from the cyclic part of the mol.

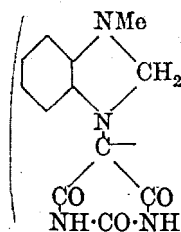
R. S. C.

Alkylacetylbarbituric acids. A. V. KIRSANOV and J. N. NASCHTSCHENKO (J. Gen. Chem. Russ., 1938, 8, 1576–1582).— $\text{COMe}\cdot\text{CH}_2\text{Br}$, NaOH, and a no. of 5-alkylbarbituric acids in aq. EtOH when heated (water-bath) yield 5-acetyl-5-methyl-, m.p. 226–228° (244–245°, 237–238°), 5-ethyl-, m.p. 234–236° (221–223°, 256–258°), 5-n-propyl-, m.p. 204–206° (210–211°, 259–260°), 5-n-butyl-, m.p. 157–158° (204–206°, 250–251°), and 5-benzylbarbituric acid, m.p. 222–223° [244–245° (decomp.), 242–244°]. The temp. in parentheses are, respectively, the m.p. of the oximes, and the m.p. (decomp.) of the phenylhydrazones. The barbituric acids described have no hypnotic, and only a feeble toxic,

action. When hydrolysed with 10% NaOH they yield the corresponding α -alkyl-lævulic acids, of which α -benzyl-lævulic acid, m.p. 65–66°, is new. Veronal and 10% NaOH yield $\text{CO}_2\text{H}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}_2$.

R. T.

Oxidative degradation of alloxan-2-dimethylaminoanil to 1-methylbenziminazole. H. RUDY and K. E. CRAMER (Ber., 1939, 72, [B], 728–744; cf. A., 1938, II, 336).—Passage of O_2 through a suspension of alloxan-2-dimethylaminoanil (I) in boiling H_2O gives *di*-5-1'-methyl-2':3'-dihydro-3'-benzimin-



azolyl-5-barbituryl ether (II), m.p. 363–365° (block; decomp.) (adducts with ZnCl_2 and HgCl_2 , slow decomp. 280–290° in bath preheated to 260°; picrate, slow decomp. >270°). (II) does not reduce AgNO_3 and does not give a colour change with H_2O_2 . It is comparatively stable towards conc. HCl. With boiling 15% NaOH it first gives a flavin

derivative, m.p. 325–330° (decomp.), and then a substance, m.p. ~210–220° (decomp.). (II) is also obtained by the condensation of $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ and alloxan in aq. EtOH. Aminodialuric acid is shown to be an intermediate product in the formation of (II) from (I). Oxidation (H_2O_2 in 50% AcOH) of (II) affords 1-methylbenziminazole (III), m.p. ~60°, b.p. 285°/740 mm. Condensation of 4-amino-5-dimethylamino-*o*-xylene with alloxan gives *di*-5-1':5':6'-trimethyl-2':3'-dihydro-3'-benziminazolyl-5-barbituryl ether, m.p. 348° (decomp.) (additive compound with ZnCl_2 and HgCl_2), also obtained by passing O_2 through a solution of alloxan-2-dimethylamino-4:5-dimethylanil in boiling 50% AcOH. 4:5-Dinitro-*o*-xylene is transformed by NHPr^i_2 in EtOH at 150–160° into non-cryst. 4-nitro-5-dipropylamino-*o*-xylene, b.p. 136–137°/2 mm., [picrate, m.p. 138° (slight decomp.)], which is reduced (Pd- CaCO_3 in MeOH) to 4-amino-5-dipropylamino-*o*-xylene, b.p. 128°/1 mm., 165°/19 mm. (picrate, m.p. 199°; hydrochloride, m.p. 170–172°; Ac derivative, m.p. 62–63°, b.p. ~152°/1 mm.). This is condensed with alloxan to *di*-5-5':6'-dimethyl-2'-ethyl-1'-propyl-2':3'-dihydro-3'-benziminazolyl-5-barbituryl ether, m.p. 384–385° (decomp.) with bath preheated to 360° (additive compounds with ZnCl_2 and HgCl_2), and dialuric acid. Parabanic acid 2-dimethylaminoanil is obtained by cautiously dissolving (I) in aq. Na_2CO_3 and adding 15% H_2O_2 followed by AcOH, the actual oxidation occurring in acid solution. It has m.p. 169° (decomp.) in a sealed tube and gives an amorphous Ag salt but does not reduce AgNO_3 . It is converted by 18.6% HCl at room temp. into a compound, decomp. <200°, probably the open form of parabanil. 15% NaOH transforms it into an unstable salt, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2\text{Na}_2$, oxidised by air followed by H_2O_2 to (III) and other compounds. Alloxan-2-dimethylamino-4:5-dimethylanil is oxidised similarly to parabanic acid 2-dimethylamino-4:5-dimethylanil (IV), red crystals which become ochre-yellow at ~215° and have m.p. 300–374° (decomp.). The substance is decolorised and decomposed by acids and alkalis. CH_2N_2 does not methylate (IV).

H. W.

Ureide, m.p. 238—239°, from alloxazine and *o*-phenylenediamine.—See A., 1939, I, 299.

Preparation of 2-alkylaminobenziminazoles. A. BLOOM and A. R. DAY (J. Org. Chem., 1939, 4, 14—19).—2-Chloromethylbenziminazole (I), m.p. 165°, is obtained in 80—85% yield by refluxing o -C₆H₄(NH₂)₂ and CH₂Cl·CO₂H with 4*N*-HCl and keeping the mixture overnight before the addition of 6*N*-aq. NH₃; if the product is worked up immediately, the yield is low (cf. Hughes and Lions, A., 1939, II, 183). Under defined conditions (I) is converted into the following dihydrochlorides of -aminomethylbenziminazole; 2-methyl-, m.p. 207—209° (decomp.); 2-ethyl-, m.p. 223—225° (decomp.); 2-butyl-, m.p. 203—204° (decomp.); 2-*n*-amyl-, m.p. 190—191° (decomp.); 2-benzyl-, m.p. 211—213° (decomp.); 2-phenylethyl-, m.p. 238—239° (decomp.). Condensation of (I) with sec.-amines in Et₂O-EtOH under defined conditions gives 2-diethyl-, m.p. 170°, 2-*di-n*-butyl-, m.p. 132°, and 2-dibenzyl-, m.p. 169°, -aminomethylbenziminazole. 2-Piperidino-, m.p. 204—205° (decomp.), and 2-morpholino-, m.p. 194—195° (decomp.), -methylbenziminazoles are obtained similarly. These do not readily give pure hydrochlorides but their stable solutions in dil. HCl are suitable for physiological testing. H. W.

Constitution of nitrosopyrrole-black. I. G. ILLARI (Gazzetta, 1939, 69, 31—40).—3-Nitroso-2-phenyl-1-methylindole, contrary to Campbell *et al.* (A., 1935, 1250), gives the Liebermann reaction, and also the NH₂OH reaction (emerald colour with the latter and β-C₁₀H₇·OH). With pyrrole in AcOH, 3-oximino-2-phenylindole gives its α-pyrrolyl ether (I), m.p. 265° (decomp.) (presumably of structure R:NR'O), which does not give either reaction, and is oxidised by K₂Cr₂O₇-H₂SO₄ to *o*-NHBz·C₆H₄·CO₂H and maleimide. Nitrosopyrrole-blacks (A., 1920, i, 397, 886) are probably similar in structure to (I), *e.g.*, (C₄H₃N)₂·NO·C₄H₄N·N·OH, or more complex condensation products. E. W. W.

Mesomerism of indigotin. B. EISTERT (Ber., 1939, 72, [B], 860; cf. van Alphen, A., 1938, II, 337).—The formulation of indigotin as a mesomeric system is due to Arndt. H. W.

Indigotin. IV. Diethoxyoxalyindigotin and the geometrical isomerism of indigotin. J. VAN ALPHEN (Rec. trav. chim., 1939, 58, 378—386; cf. A., 1939, II, 229).—Examples are given of the ready formation of derivatives of *cis*-indigotin. Indigotin, CO₂Et·COCl, and C₅H₅N (room temp.) give oxalyindigotin (yellow) and 1:1'-diethoxyoxalyindigotin (dark cherry-red), decomposed by heat or by EtOH-NH₃ or -NH₂Ph into Et₂C₂O₄ and oxalyindigotin. Similarly indigotindianil gives oxalyindigotindianil (violet-red) and 1:1'-diethoxyoxalyindigotindianil (decomp. 125°). S. H. H.

Alkylamino-derivatives of 6-nitro- and 6-chloro-quinazolines. O. J. MAGIDSON and E. S. GOLOVTSCHINSKAJA (J. Gen. Chem. Russ., 1938, 8, 1797—1809).—4-Chloroquinazoline and NH₂·[CH₂]₃·NEt₂ (I) in Et₂O yield 4-(γ-diethylaminopropyl)aminoquinazoline, b.p. 215—220°/0.8 mm. (di-oxalate, m.p. 135°; picrate, m.p. 199—201°). 5-

Chloroanthranilic acid and HCO·NH₂ at 135° give 5-chloro-*N*-aminohydroxymethylanthranilic acid, m.p. 179°, which at 185—190° condenses, to yield 6-chloro-3:4-dihydro-4-quinazoline, m.p. 263—265°; this, heated with PCl₅ and POCl₃ (75 min. at the b.p.), yields 4:6-dichloroquinazoline, m.p. 155—156°, which with (I) or α-diethylamino-δ-aminopentane (II) affords 6-chloro-4-(γ-diethylaminopropyl)- (dihydrochloride, m.p. 255°; picrate, m.p. 181—184°) or 6-chloro-4-(δ-diethylamino-α-methylbutyl)-aminoquinazoline, m.p. 107—110° (dioxalate, m.p. 185°). 5-Chloro-3-nitroacet-*o*-toluidide is oxidised (KMnO₄) to 5-chloro-3-nitroacetanthranilic acid, m.p. 171—172°, hydrolysed by 20% HCl (5 hr. at 110°) to 5-chloro-3-nitroanthranilic acid, m.p. 237—238°. Formylanthranilic acid in H₂SO₄ and HNO₃ yield 5-nitroformylanthranilic acid, m.p. 225—230°, readily hydrolysed by H₂O to 5-nitroanthranilic acid, which with HCO·NH₂ (4 hr. at 150—160°) gives 6-nitro-3:4-dihydro-4-quinazoline (III), m.p. 282°, also obtained by nitration of 4-quinazoline. (III) and POCl₃-PCl₅ (2 hr. at the b.p.) give 4-chloro-6-nitroquinazoline, which with (II) affords 6-nitro-4-(δ-diethylamino-α-methylbutyl)aminoquinazoline, m.p. 126—127°, reduced by (NH₄)₂S in EtOH to the corresponding 6-NH₂-compound, m.p. 89—91° (picrate, m.p. 204—205°; sulphate, m.p. 168—169°). This heated at 130—140° with Ph₂CO₃ affords bis-[4-(δ-diethylamino-α-methylbutyl)amino-6-quinazolyl]carbamide, decomp. 170—185°. The various products described above had no anti-malarial action. R. T.

Quinazolines. XLIV. Synthesis of new quinazoline derivatives of veratrole akin to alkaloids. C. A. FETSCHER and M. T. BOGERT (J. Org. Chem., 1939, 4, 71—87).—Slow addition of 4-chloroveratrole to HNO₃ (*d* 1.4) at room temp. gives 4-chloro-5-nitroveratrole, m.p. 118° (corr.) (yield 95%), converted by NH₃-EtOH at 130° into 5-nitro-4-aminoveratrole, m.p. 171° (corr.). 4-Nitroveratrole and boiling SO₂Cl₂ afford 6-chloro-4-nitroveratrole, m.p. 95° (corr.), which does not react with NH₃ or alkylamines. It is reduced by Sn containing a trace of graphite and 50% HCl to 6-chloro-4-aminoveratrole, m.p. 89° (corr.). 4-Amino-veratrole, m.p. 86°, is best obtained by catalytic reduction (Pt) of the 4-NO₂-compound; its hydrochloride (I), m.p. 240° (corr.), darkens rapidly when exposed to air and light. It could not be formylated but readily gives *Ac*, m.p. 133° (corr.), *Bz*, m.p. 178° (corr.), and *oxalyl*, m.p. 168° (corr.), derivatives. CO(NH₂)₂ in boiling H₂O transforms (I) into 3:4-dimethoxyphenylcarbamide (II), m.p. 210° (corr.), which is tasteless though structurally related to dulcin, *s*-, m.p. 313° (corr.), and *as*-, m.p. 219° (corr.), -*di*-3:4-dimethoxyphenylcarbamide. With AcCl in C₅H₅N at 0° (II) yields 3-acetyl-3:4-dimethoxyphenylcarbamide, m.p. 227° (corr.), which passes into a brown gum when heated above its m.p. and is unchanged by P₂O₅ in boiling PhMe or xylene. Analogous behaviour is shown by *s*-phenylacetyl-3:4-dimethoxyphenylcarbamide, m.p. 249° (corr.), and by the corresponding homoveratroyl compound, m.p. 256° (corr.). Veratryl chloride reacts vigorously with Mg in Et₂O but the resulting product is indifferent to COMe₂ or H₂O. Passage of dry HCl through a cooled mixture of veratrole, paraformaldehyde, and fused ZnCl₂ affords

mainly 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene, m.p. 235° (corr.). HNO_3 (*d* 1.4) converts veratraldehyde at 15–25° in semi-darkness into 6-nitroveratraldehyde, m.p. 133° (corr.). It appears to react normally with MgPhBr . It is transformed by dry HCl and $\text{HCO}\cdot\text{NH}_2$ into 6-nitroveratrylidenediformamide, m.p. 195.5° (corr.), which is converted by Zn dust and AcOH into 6 : 7-dimethoxyquinazoline, m.p. 143° (corr.) [hydrochloride, m.p. 227° (corr.)]. 6-Nitroveratric acid, m.p. 189–190° (corr.) [Et ester (III), m.p. 99.5° (corr.)], is transformed by SOCl_2 in CHCl_3 at room temp. into the chloride, m.p. 88–89° (corr.), whence the amide, m.p. 193° (corr.), and nitrile, m.p. 168° (corr.), which could not be caused to react with MgBuBr or MgPhBr . Hydrogenation (PdCl_2 in EtOAc) of (III) affords *Et* 6-nitroso- or 6-oximinoveratrate, m.p. 70° (corr.). EtOAc_2 , (III), and Na wire give *Et* 6-nitroveratroylacetate, m.p. 73° (corr.), the Na derivative of which could not be caused to condense with PhCl , PhBr , 4-chloro-, 4-bromo-, or 4-iodoveratrole. 6-Nitroveratroylacetic acid, m.p. 219° (corr.), is slowly changed by boiling aq. $\text{Ba}(\text{OH})_2$ and the product is converted by steam-distillation in the presence of HCl into chloronitroaceto-vanillone or isovanillone, m.p. 165° (corr.). *Et* 6-aminoveratrate, m.p. 88° (corr.), best obtained by catalytic reduction (Adams) of (III), is transformed by HCO_2Et at 130° into *Et* 6-aminoveratroylformate, m.p. 70° (corr.), which does not yield a quinazoline when boiled with aq. NH_3 but gives CO , CO_2 , 6-aminoveratraldehyde, and 6-aminoveratric acid; its constitution is proved further by its conversion by 10% KOH at 40° into 5 : 6-dimethoxyisatin, m.p. ~180–195°. *Et* 6-acetamidoveratrate, m.p. 130° (corr.), is unaffected when heated with Na and EtOAc in large excess. 6-Acetamidoveratric acid, m.p. 233° (corr.), and Ac_2O give 6 : 7-dimethoxyacetanthranil, transformed by boiling 10N-aq. NH_3 containing a little KOH into 6 : 7-dimethoxy-2-methyl-4-quinazolone, m.p. 312° (corr.). 6-Phenylacetamidoveratric acid, m.p. 226° (corr.), is similarly converted into 6 : 7-dimethoxy-2-benzyl-4-quinazolone, m.p. 253° (corr.), and 6-homoveratroylamidoveratric acid, m.p. 241° (corr.), into 6 : 7-dimethoxy-2-veratryl-4-quinazolone, m.p. 269° (corr.). Na homoveratrate and 6-nitroveratraldehyde in Ac_2O at 105° give 6'-nitro-3 : 4-dimethoxy- α -3' : 4'-dimethoxyphenylcinnamic acid, m.p. 187° (corr.), which gives oily products when heated with AcOH saturated with HBr at 90–100°. Attempted nitration of veratroin leads to veratril, which could not be satisfactorily nitrated. 1 : 2 : 3 : 4-Tetrahydroquinazoline is best obtained from quinazoline by reduction with 4% Na-Hg .

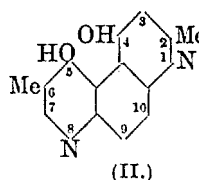
H. W.

Pyrazole derivatives. T. N. GHOSH and D. DAS-GUPTA (J. Indian Chem. Soc., 1939, 16, 63–66). —4-Phenylhydrazonoacetyl-1-phenyl-3-methyl-5-pyrazolone (prep. from the diketone by 1 mol. of $\text{NHPh}\cdot\text{NH}_2$ in EtOH), m.p. 197°, is converted by ZnCl_2 into 1-phenyl-4 : 2'-indolyl-3-methyl-5-pyrazolone, sinters at 225°, m.p. 238° (decomp.), or by HCl -abs. EtOH into 1 : 1'-diphenyl-3 : 3'-dimethylpyrazolo-4 : 5-4' : 5'-pyrazole, softens at 123°, m.p. 129–130°. 4-Amino-1-phenyl-3-methyl-5-pyrazolone and CH_3Ac_2 alone at 100° give 5% or in AcOH-H_2 gives 10% of 3-acetyl-

1'-phenyl-2 : 3'-dimethylpyrazolo-4 : 5-5' : 4'-pyrazole, m.p. >320° (:CHPh derivative, m.p. >300°).

R. S. C.

Extension of the Conrad-Limpach reaction to the *p*-phenanthroline series. G. JACINI (Gazzetta, 1939, 69, 111–117). — $\text{p-C}_6\text{H}_4(\text{NH}_2)_2$ in boiling $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ (I) gives *Et*, *p*-phenylenebis- β -aminocrotonate (A., 1936, 64), which in paraffin oil at 260° gives 4 : 5-dihydroxy-2 : 6-dimethyl-1 : 8-phenanthroline



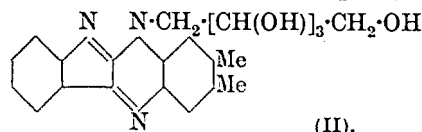
(II), m.p. 332° [*Ba* salt; picrate, m.p. 290° (decomp.); *Me*, ether, m.p. 234.5° (decomp.); phthalate]. The structure of (II) is established by synthesis from

$\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, which with (I) gives *Et* β -*p*-acetamidoanilino-crotonate, m.p. 182°, converted at 260°

into the *N*-Ac derivative, m.p. 352°, of 6-amino-4-hydroxy-3-methylquinoline, m.p. 312°, thence into *Et* β -4-hydroxy-2-methyl-6-quinolylaminocrotonate, m.p. 160°, and this at 260° into (II).

E. W. W.

Isatin, alloxan, and their derived azines. L. MARCHLEWSKI (Rocz. Chem., 1938, 18, 698–717). —Aq. alloxan (I) and $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ (2 hr. at 100°) yield 3-carbamylcarbamy-2-hydroxyquinoxaline, m.p. 238–239°, the mol. extinction curve of which differs considerably from that of (I), but is similar to that of alloxazine. Mol. extinction curves are given for indophenazine, 1-hydroxy-2-*o*-aminophenylquinoxal-



ine, coumarophenazine, and 1-ribityl-6 : 7-dimethyl-2 : 3-indoquinoxaline (II) (prepared by condensing 2-ribosamido-4 : 5-dimethylaniline with isatin, in AcOH).

R. T.

Synthesis of compounds of the 2'-phenylquinolino-4' : 3'-2 : 3-quinoline type. K. DZIEWOŃSKI and E. CHOLEWA (Bull. Acad. Polonaise, 1938, A, 551–555). — $\text{C}(\text{NPh})_2$ and COPhMe at 200–250° give 2'-phenylquinolino-4' : 3'-2 : 3-quinol-4-oneanil, m.p. 247–248°, by way of 4-anilino-2-phenylquinoline (not isolated), which reacts further with PhNCO formed during the reaction. $\text{C}(\text{NPh})_2$ and $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ at 250–270° give 2'-*p*-tolylquinolino-4' : 3'-2 : 3-quinol-4-oneanil, m.p. 222–223° [picrate, m.p. 238–239° (decomp.); *NO*-derivative, m.p. 143–144° (decomp.)], which with hot HCl - AcOH gives 2'-*p*-tolylquinolino-4' : 3'-2 : 3-quinol-4-one (I), m.p. 364°, and with KOH - EtOH at 190–200° gives 4-hydroxy-2'-*p*-tolylquinolino-4' : 3'-2 : 3-quinoline (II), m.p. 331–333°. (I) is converted into (II) by KOH , and (II) into (I) by HCl .

R. S. C.

Uric acid and cyanuric acid. The carbamyl group. H. BILTZ (Ber., 1939, 72, [B], 807–818). —The tautomerism and mesomerism of uric acid and of cyanuric acid are discussed with special reference to the work of Fromherz *et al.* (A., 1936, 1317; 1937, II, 36), the author agreeing with Arndt and Eistert (A., 1939, II, 36) that there is no discrepancy between the chemical evidence and that from ultra-violet

absorption spectra when due account is taken of the mesomerism of the grouping $\cdot\text{CO}\cdot\text{NH}\cdot$ and of the anion, and of the way in which these are influenced by the structure of the ring as a whole. The following generalisations are illustrated by a wide range of examples: H in the simple grouping $\cdot\text{CO}\cdot\text{NH}\cdot$ is not acidic, but becomes acidic in $\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot$ without, however, having any tendency to enolisation except where two special conditions are fulfilled, viz., that the C:N linking should be able to form part of a conjugated system with double linkings actually (as distinct from potentially) present, and that it should be the last double linking which could be formed in the ring. These conditions hold for the five-ring, but not for the six-ring, in uric acid.

F. J. G.

isoGuanine sulphate.—See A., 1939, III, 536.

Isomerisation of benzylidene derivatives. I.

H. S. JOIS, A. KUPPUSAMI, and B. L. MANJUNATH (J. Indian Chem. Soc., 1939, **16**, 43—46; cf. Proc. Indian Sci. Congress, 1930, 163).—1 : 3 : 4 : 6-

$(\text{NH}_2)_2\text{C}_6\text{H}_2(\text{NHPh})_2$ (I) and PhCHO in boiling EtOH readily give the red *dibenzylidene* derivative, m.p. 168°, which when refluxed in EtOH (2 hr.) isomerises

with ring-closure, to the yellow *dibenzylidenehydrophenazine* [1' : 10'-*dibenzyl*-1' : 4' : 5' : 10'-*tetrahydroquinoxalino*-(2' : 3' : 2 : 3)-*phenazine*] derivative [(A), R = CH_2Ph], m.p. 282–5°.

Similarly, the *disalicylidene*, m.p. 204°, *dianisylidene*, m.p. 176°, *divanillylidene* (not isolable), *dipiperonylidene*, m.p. 162–169° (isomerises during purification), and *dicinnamylidene*, m.p. 184–5°, derivative of (I) are converted (at varying rates) into the corresponding *dihydrophenazines*, m.p. 329°, 294–5°, 313–5°, 291°, and 296°, respectively. CH_2O and MeCHO give resins. 4 : 6 : 1 : 3- $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)_2$ (II) and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ at 150° afford 1 : 3-*dinitro*-4 : 6-*di-o-toluidinobenzene*, m.p. 198°, reduced (NaHS) to the 1 : 3-*diamine*, m.p. 186°, the $(\text{CHPh})_2$, m.p. 147°, *disalicylidene*, m.p. 188°, *divanillylidene* (not isolable), and *dipiperonylidene*, m.p. 179°, derivatives of which are isomerised to the corresponding *phenazine* derivatives (as A), m.p. 262°, 305°, 306°, and 285°, respectively. Mesidine and (II) give 1 : 3-*dinitro*-4 : 6-*dimesidinobenzene*, m.p. 201°, reduced to the 1 : 3-*diamine*, m.p. 152°, the $(\text{CHPh})_2$ derivative, m.p. 119°, of which does not isomerise in EtOH (16 hr.) (required positions for ring-closure blocked).

A. T. P.

L-Cystine from porphyrin c. H. THEORELL (Enzymologia, 1939, **6**, 88).—Porphyrin c (I) with HBr-AcOH yields a coloured product and an aq. solution from which, by pptn. with $\text{Hg}(\text{OAc})_2$, L-cystine is isolated. The formulation of (I) is therefore completed (cf. A., 1938, II, 462) by two $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{S}\cdot$ groups.

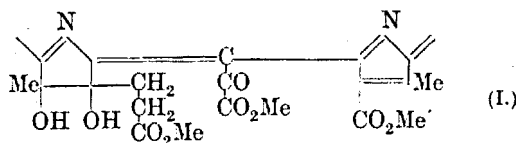
F. O. H.

Chlorophyll. LXXXVI. *Acetyl rhodin g₇* and certain *vinylporphyrins*. H. FISCHER, A. OESTREICHER, and A. ALBERT (Annalen, 1939, **538**, 128—143).—Rhodin *g₇* Me₃ ester is converted by HBr-AcOH at room temp. into the non-cryst. 2- α -

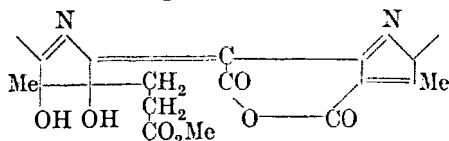
bromomesorhodin g₇, which is hydrolysed by 20% HCl to 2- α -*hydroxymesorhodin g₇*, m.p. 185°. This is oxidised by finely-divided $\text{Na}_2\text{Cr}_2\text{O}_7$ in $\text{C}_5\text{H}_5\text{N}$ to 2-*acetyl rhodin g₇*, m.p. 263°. Methylphæophorbide *a* in boiling HCO_2H containing a little Fe powder passes (with after-treatment with CH_3N_2) into *vinylphæoporphyrin a₅ Me₂ ester* (I), m.p. 288–292°. It readily gives poorly cryst., complex salts of which the *phyllin*, *hæmin*, $\text{C}_{36}\text{H}_{34}\text{O}_5\text{NFeCl}$, which gives the spectrum of phæoporphyrin *a₅* (II) when treated with 80% H_2SO_4 , and Cu compound, $\text{C}_{36}\text{H}_{34}\text{O}_5\text{N}_4\text{Cu}$, m.p. > 320°, are described; only with $\text{Fe}(\text{OAc})_2\cdot\text{HCl}$ is the original vinyl compound apparently regenerated. NH_2OH , HCl, anhyd. KOAc, and (I) in $\text{C}_5\text{H}_5\text{N}$ give a well-defined *oxime*, m.p. 286°. The constitution of (I) is further established by its ready transformation into (II) under various conditions and by its conversion by KOH in MeOH- $\text{C}_5\text{H}_5\text{N}$ into *vinylchloroporphyrin e₆ Me₃ ester*, m.p. 234°, also obtained from chlorin *e₆ Me₃ ester*, 80% HCO_2H , and a little Fe; this yields a Cu complex, m.p. 222°. $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ is added to a well-crystallised D.E.E.-phæoporphyrin *a₅*. (I) can be prepared by treatment of 10-acetoxymethylphæoporphyrin *a₅* (II) with conc. H_2SO_4 at 0° followed by reduction of the 10-hydroxymethylphæoporphyrin *a₅* so formed with 100% HCO_2H or by AlCl_3 in anhyd. CHCl_3 . Mild hydrolysis of (II) with KOH-MeOH gives *vinylphæoporphyrin a₇*, m.p. 274–276°, in 20% yield. Pyrophæophorbide *a* is transformed by $\text{HCO}_2\text{H}\cdot\text{Fe}$ into *vinylphyloerythrin*, m.p. 278° (additive compound with $\text{CHN}_2\cdot\text{CO}_2\text{Et}$).

H. W.

Chlorophyll. LXXXVII. Partial oxidation of chlorophyll derivatives. H. FISCHER and M. CONRAD (Annalen, 1939, **538**, 143—156).—Dihydroxychlorin *e₆ Me₃ ester* is converted by KOH-Pr^oOH in $\text{C}_5\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$ followed by 10% and 15% HCl into *dihydroxypurpurin 7 Me₂ ester* (I), m.p. 158° (which



(I.)



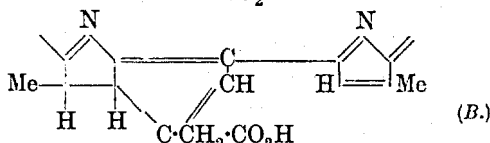
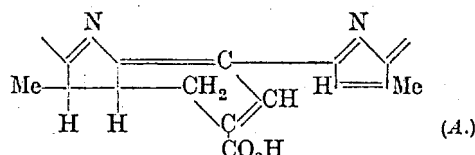
(II.)

resembles 2-acetyl purpurin 7 in spectrum, decomposes in boiling $\text{CHN}_2\cdot\text{CO}_2\text{Et}$, and passes in boiling $\text{C}_5\text{H}_5\text{N}$ into vinylrhodoporphyrin, and under somewhat different conditions into *dihydroxypurpurin 18 Me ester* (II), m.p. 235°, which resembles 2-acetyl purpurin 18 in spectrum. The existence of (I) and (II) supports the open formula for purpurin 7 since a furan ring is here impossible. Mesophæophorbide *b* is similarly converted into *b-mesopurpurin 7 Me₃ ester*, m.p. 239°. The reaction fails with pyrophæophorbide *b* (III) when KOH-Pr^oOH is used. In the *a* series ring fission occurs and, from a complex mixture, adsorption on talc yields small amounts of rhodochlorin, m.p. 210°, much more readily obtained by oxidising phæophorbide *a* (IV) with H_2O_2 in $\text{C}_5\text{H}_5\text{N}$.

dioxan. Oxidation with CrO_3 - AcOH transforms (III) into *dihydroxypyrophæophorbide b ester*, m.p. 202° . Reaction is not always reproducible and is best effected with H_2O_2 in dioxan. Treatment of (IV) with NH_2Me and of the product with $\text{KOH-Pr}^n\text{OH}$ gives an unstable *chlorin*, $\text{C}_{33}\text{H}_{34}\text{O}_5\text{N}_4$, m.p. $>320^\circ$, which does not react with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ and is degraded by HI to a mixture from which chloroporphyrin is extracted. Esterification of it with CH_2N_2 yields purpurin e_5 , m.p. 189° , converted by boiling $\text{C}_5\text{H}_5\text{N}$ into vinylrhodoporphyrin, m.p. 280° . With N_2H_4 in $\text{C}_5\text{H}_5\text{N-Et}_2\text{O}$ at room temp. methylphæophorbide a gives a *chlorin*, $\text{C}_{36}\text{H}_{42}\text{O}_5\text{N}_6$, m.p. 195° after decomp. at 145° , which resembles chlorin e_6 spectroscopically. (IV) is transformed by $\text{CH}_2\text{Ph-NH}_2$ in $\text{C}_5\text{H}_5\text{N}$ into *chlorin e}_8* $\gamma\text{-Me}_1$ ester 6-carboxbenzylamide, m.p. 175° ; this is not effected by protracted boiling with $\text{Na}_2\text{CO}_3\text{-C}_5\text{H}_5\text{N}$ or short boiling with $\text{KOEt-C}_5\text{H}_5\text{N}$ under N_2 . It gives a somewhat indefinite purpurin 7, degraded to *vinylrhodoporphyrin Me}_2* ester, m.p. 282° . It is converted by I and Na_2CO_3 in boiling $\text{CHCl}_3\text{-MeOH}$ into phæoporphyrin a_7 , m.p. 256° . Passage of air through a solution of (I) in 1% NaOH at 50° and extraction of an Et_2O solution of the product with 10% HCl affords rhodin g_7 , identified as the Me_3 ester, m.p. 247° ; with more conc. acid b -purpurin 7 results, converted by boiling $\text{C}_5\text{H}_5\text{N}$ into b -vinylrhodoporphyrin. Rhodin g_7 and MeNO_2 in $\text{C}_5\text{H}_5\text{N}$ containing a little piperidine give the compound, $\text{C}_{38}\text{H}_{41}\text{O}_8\text{N}_5$, m.p. 205° . Rhodin g_7 Me_3 ester Me acetal, m.p. 174° , is incidentally described. H. W.

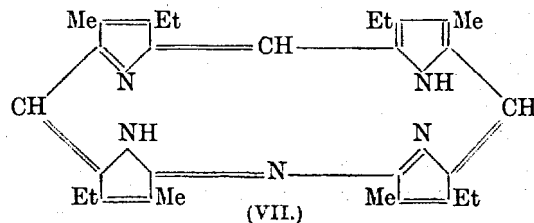
Neopurpurins. H. FISCHER and M. STRELL (Annalen, 1939, 538, 157—171).—Purpurin-5 Me_2 ester in $\text{C}_5\text{H}_5\text{N}$ is transformed by 25% $\text{KOH-Pr}^n\text{OH}$ at room temp. followed by treatment with CH_2N_2 into *neopurpurin 4* (I), $\text{C}_{35}\text{H}_{38}\text{O}_4\text{N}_4$, m.p. 227° , $[\alpha]_{\text{D}}^{20} -555^\circ$ in COMe_2 , which is little affected by Ag_2O in $\text{C}_5\text{H}_5\text{N}$ or by evaporation with HCO_2H . In $\text{CHN}_2\text{-CO}_2\text{Et}$ at 100° the spectrum becomes displaced towards the blue. It is hydrogenated (Pd in dioxan) to *mesoneopurpurin 4*. It gives a Cu complex. It is isomerised by HI in AcOH to a porphyrin, $\text{C}_{35}\text{H}_{38}\text{O}_4\text{N}_4$, m.p. 228° , which gradually decomposes at $>300^\circ$, is scarcely affected by boiling $\text{Na}_2\text{CO}_3\text{-C}_5\text{H}_5\text{N}$ or AcOH , and affords a Cu complex, m.p. 268° . 30% KOH-MeOH at 100° transforms (I) into vinylrhodoporphyrin, 2-ethyl- and 2-vinylporphyrin; the last-named when boiled with $\text{CHN}_2\text{-CO}_2\text{Et}$ has its spectrum displaced towards the blue. γ -Formylpyrrochlorin [purpurin 3 Me_2 ester] is converted by 5% KOH-MeOH in $\text{C}_5\text{H}_5\text{N}$ and subsequent esterification into *neopurpurin 2* (II), $\text{C}_{38}\text{H}_{38}\text{O}_4\text{N}_4$, m.p. 253° , $[\alpha]_{\text{D}}^{20} -1100^\circ$ in exluan . It is decomposed by 25% KOH-MeOH at 100° . Its spectrum is displaced towards the blue by $\text{CHN}_2\text{-CO}_2\text{Et}$. Hydrogenation (Pd in dioxan) of it gives *mesoneopurpurin 2*. The Cu complex is described. Hydrolysis with KOH-MeOH followed by treatment with AcOH of (I) affords (II). The *neopurpurin* reaction appears proper to the chlorin system; analogous experiments with γ -formylpyrroporphyrin and chloroporphyrin e_5 diazomethane ester were unsuccessful. The responsibility for the change rests with the γ -formyl group, which is absent in (I) and (II) as shown by negative results of attempted oximation.

CO_2H at 6 takes no part in the change. Reasons are



advanced for considering the arrangement A or B to be characteristic of the *neopurpurins*. H. W.

Imidoporphyrins. V. New synthesis of monoimidoporphyrins and further modes of formation of di- and tetra-imidoporphyrins. F. ENDERMANN and H. FISCHER (Annalen, 1939, 538, 172—194; cf. A., 1937, II, 471).—2-Formyl-4-methyl-3-ethylpyrrole-5-carboxazide is converted by boiling abs. EtOH into 5-urethano-2-formyl-4-methyl-3-ethylpyrrole (I), $\text{CHO}\cdot\text{C}(\text{Me})=\text{NH}\cdot\text{C}(\text{NH}\cdot\text{CO}_2\text{Et})$, m.p. 133° (oxime, m.p. 167°). 2:4-Dimethyl-3-ethylpyrrole-5-carboxazide in Et_2O is transformed by SO_2Cl_2 at room temp. into an unstable Cl_3 -derivative, converted by EtOH at 0° into 2-carbethoxy-4-methyl-3-ethylpyrrole-5-carboxazide, decomp. $99\text{--}100^\circ$, which with boiling abs. EtOH yields 5-urethano-2-carbethoxy-4-methyl-3-ethylpyrrole (II), decomp. 102° . Et 2:3-dimethyl-4-ethylpyrrole-5-carboxylate and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 145° give 2:3-dimethyl-4-ethylpyrrole-5-carboxyhydrazide, m.p. 187° , converted by $\text{NaNO}_2\text{-AcOH}$ into the corresponding azide, decomp. 118° ; this is transformed by SO_2Cl_2 in abs. EtOH at room temp. followed by $\text{MeOH-H}_2\text{O}$ into the unstable formyl compound, decomp. 110° , converted by boiling abs. EtOH into 5-urethano-2-formyl-3-methyl-4-ethylpyrrole (III), decomp. $185\text{--}187^\circ$, which passes into $\alpha\gamma$ -di-imidoætioporphyrin II when heated above its m.p. (I) and cryptopyrrole are converted by 48% HBr in EtOH into 5-urethano-4:3':5'-trimethyl-3:4'-diethylpyrromethene hydrobromide (IV), decomp. $180\text{--}185^\circ$ [free base, m.p. 145° (decomp.)]. With hæmopyrrole (I) gives 5-urethano-4:4':5'-trimethyl-3:3'-diethylpyrromethene hydrobromide (V), decomp. 189° (free base, decomp. $128\text{--}129^\circ$), and (III) affords 5-urethano-3:4':5'-trimethyl-4:3'-diethylpyrromethene hydrobromide (VI), decomp. $177\text{--}178^\circ$ (free base, m.p. 124°). Treatment of (IV), (V), and (VI) with Br-AcOH at 100° followed



by NaOH in boiling quinoline gives respectively γ -monoimidoporphyrin IV, (VII), m.p. $>300^\circ$,

β (δ)-monoimidoetioporphyrin II, and α -monoimidoetioporphyrin IV, all of which have the same spectrum in Et₂O. The "autoxidised urethane" obtained by heating 2:4-dimethyl-3-ethylpyrrolecarboxazide with EtOH is converted by hot NHPH-NH₂ into β δ -di-imidoetioporphyrin (VIII), and in addition, into a *monoimidoporphyrin* and β δ -di-imidoetioporphyrin II (IX), distinguished from (VIII) in spectrum and by its greater basicity. 2:3-Dimethyl-4-ethylpyrrole-5-carboxazide in boiling abs. EtOH passes into an autoxidised urethane, C₁₁H₁₈O₃N₂, m.p. 142°, transformed by NHPH-NH₂ at 220° into a mixture of mono- and di-imidoetioporphyrin of the unsymmetrical type. 3-Methyl-4-ethylpyrrole-2:5-dicarboxazide is converted by Zn dust and AcOH at room temp. into 3-methyl-4-ethylpyrrole-2:5-dicarboxylamide, decomp. 261°, by 50% AcOH at 100° into 2:5-diamino-3-methyl-4-ethylpyrrole (*picrate*, m.p. 195—196°), and by boiling PhMe or xylene into 3-methyl-4-ethylpyrrole-2:5-dicarbimide, decomp. 266°, converted by NMe₄-OH in boiling C₆H₅N into tetraimidoetioporphyrin, m.p. 262°. Oxidation of (IX) by CrO₃ in H₂SO₄ at 0° affords methylethylmaleimide. The known imidoporphyrins are obtained as cryst. compounds the colour of which darkens with increasing N content. Their solutions in org. media have an intense red fluorescence. The basicity diminishes with increasing N content, the mono-, di- (sym. type), and tetra-compounds being extractable from Et₂O by 9—12%, 18—22%, and conc. HCl respectively. In contrast to the porphyrins they are stable towards light in the presence of alkoxide. H. W.

Formation of benzoxazoles from o-amino-phenols. W. THEILACKER (J. pr. Chem., 1939, [ii], 153, 54—56).—1-Methylbenzoxazole is obtained (a) by boiling o-NH₂-C₆H₄-OH with Ac₂O and then distilling the mixture or (b) by heating o-NHAc-C₆H₄-OAc at 190° (slowly) or 210° (rapidly) (cf. A., 1938, II, 485). The diacyl derivative is thus an intermediate in the formation of benzoxazoles.

R. S. C.

Special case of isomerism. M. BETTI (Roc. Chem., 1938, 18, 350—354; cf. A., 1915, i, 896, 997; 1916, i, 222).—3:5-Diphenylisooxazole-4-carboxylamide yields 3:5-diphenylisooxazole-4-carboxylic acid, m.p. 233° (chloride, m.p. 89°; amide, m.p. 229°; anilide, m.p. 188°; Et ester, m.p. 52°), when hydrolysed with conc. aq. NaOH, and an isomeric acid, m.p. 153° (chloride, an oil; amide, m.p. 229°; anilide, m.p. 236°; Et ester, an oil), when hydrolysed with dil. aq. NaOH. The nature of this case of isomerism is not clear. R. T.

Thiamin [aneurin] analogues. I. β -4-Methyl-5-thiazolylalanine. E. R. BUCHMAN and E. M. RICHARDSON (J. Amer. Chem. Soc., 1939, 61, 891—893).—CHCl₃Ac-CO₂Me (prep. from CH₃Ac-CO₂Me by SO₂Cl₂) and HCS-NH₂ in a little EtOH at 0—25° give 58% of Me 4-methylthiazole-5-carboxylate, which yields the *hydrazide*, m.p. 166°. The PhSO₂ derivative, m.p. 170°, thereof with anhyd. Na₂CO₃ in (CH₃)₂CO at 160° gives 4-methylthiazole-5-aldehyde, m.p. 75°, b.p. 112—118°/21 mm. (*phenyl*-, m.p. 158—159°, and *dinitrophenyl-hydrazone*, m.p. >235°), con-

verted into the *azlactone*, m.p. 199—200°, and thence (NaOH) into α -benzamido- β -4-methyl-5-thiazolylacrylic acid, m.p. 217°, reduced by HI-Ac₂O-red P to β -4-methyl-5-thiazolylalanine (I), +0.5H₂O, decomp. ~237°. Pea-roots, but not *Phycomyces Blakesleeanus* or *S. aureus*, use (I) as a source of vitamin-B₁.

R. S. C.

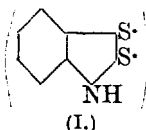
Benzthiazoles.—See B., 1938, 533.

Arylpyridines. X. Thiazole derivatives. H. PASSING (J. pr. Chem., 1939, [ii], 153, 1—25).—Purely aromatic *sec.* amines are too feebly basic to give carbamides in aq. media, but do so when converted into hydrochlorides by dry HCl in PhCl or o-C₆H₄Cl₂ and then heated with NH₄SCN at 100°. The carbamides and Br in CHCl₃ give the carbenium bromides, [NArR-C+(NH₂)-SBr]Br⁻, which spontaneously lose HBr to give the 1-aminobenzthiazolanium bromides, [C₆H₄<S<NR>C⁺·NH₂]Br⁻, and then lose a second HBr when treated with alkali, yielding 1-iminobenzthiazolines. These are converted by aq. NaNO₂ in AcOH into the N-NO-derivatives, which decompose exothermally in hot xylene into 1-ketobenzthiazolines. These CO-derivatives with aliphatic or aromatic Mg halides give mercaptans and compounds which with HClO₄ yield deep-coloured salts; with CH₂Ph·MgCl, however, they yield 1-benzylbenzthiazolanium salts, which do not give the 1-OH-compounds but with C₆H₅N or with alkali in COMe₂ or EtOH give the 1-benzylidenethiazolidines. The following are described. NN-Diphenylthiocarbamide, m.p. 210° (decomp.); N-phenyl-, m.p. 224° (decomp.), N-p-tolyl-, dimorphic, m.p. 193° (decomp.) and 176° (unstable), and N-p-anisyl-, m.p. 216° (decomp.), β -naphthylthiocarbamide; NN-di-p-hydroxyphenylthiocarbamide, m.p. 232° (decomp.), does not give a thiazole. 1-Amino-2-phenylbenzthiazoline 1-bromide, m.p. 272° (decomp.); 2-amino-3-phenyl-, m.p. 278° (decomp.), -3-p-tolyl-, m.p. 276° (decomp.), and -3-p-anisyl-, m.p. 284° (decomp.), -naphtha-1':2':5:4-thiazoline 2-bromide. 1-Imino-2-phenylbenzthiazoline, m.p. 74—75° (NO-derivative, decomp. 141°); 2-imino-3-phenyl-, m.p. 134—135° (decomp.) (NO-derivative, decomp. 156°), -3-p-tolyl-, m.p. 129° (NO-derivative, decomp. 144°), and -3-p-anisyl-, m.p. 181—182° (NO-derivative, decomp. 145°), -naphtha-1':2':5:4-thiazoline. 2-Methyl-, m.p. 76°, b.p. 164°/14 mm., and 2-phenyl-benzthiazol-1-one, m.p. 81—82°, b.p. 227°/16 mm. (forms no oxime or semicarbazone); 3-phenyl-, m.p. 144—145°, 3-p-tolyl-, m.p. 170—171°, 3-p-anisyl-, m.p. 157—158°, 3-ethyl-, m.p. 134—135° (lit. 124°), b.p. 234°/14 mm., and 3-p-hydroxyphenyl-, m.p. 214—215°, -naphtha-1':2':5:4-thiazol-2-one. 2-Phenyl-1-benzyl-, m.p. 216—217°, 1-benzyl-2-methyl-, m.p. 168—169° (decomp.) (lit. 146°), and 2-methyl-1-ethyl-, m.p. 199—201° (decomp.), -benzthiazolanium perchlorate; 3-phenyl-, m.p. 227—299° (decomp.), 3-p-tolyl-, m.p. 224—226° (decomp.), 3-p-anisyl-, m.p. 207—210° (decomp.), and 3-p-hydroxyphenyl-, m.p. 246—248° (decomp.), -2-benzyl-naphtha-1':2':5:4-thiazolanium perchlorate; 3-p-anisyl-2-methyl-, m.p. 233—235°, and 2-benzyl-3-ethyl-, m.p. 207—208° (decomp.), -naphtha-1':2':5:4-thiazolanium perchlorate. 2-Phenyl-1-benzylidenbenzthiazoline, m.p. 129—

131° (decomp.); 3-phenyl-, m.p. ~108° (after sintering), 3-p-tolyl-, m.p. 145—147° (decomp.), and 3-p-anisyl-, m.p. 153—154°, 2-benzylidenenaphtha-1':2'-5:4-thiazoline; 2-benzylidene-3-ethylnaphtha-1':2'-5:4-thiazoline, m.p. 175—176° (decomp.). N-Anisyl-β-naphthylamine, m.p. 104°, b.p. 261°/13 mm., is prepared from the OH-amine by Me₂SO₄-aq. NaOH at 100° under N₂. R. S. C.

Action of sulphur on organic compounds.

XIII. L. SZPERL (Rocz. Chem., 1938, 18, 804—811).—Pyrrole and coumarone undergo profound decomp. when heated with S. Indole and S (52 hr. at 150—160°) yield the substance (I), m.p. 298—298.5°, together with a substance, C₁₆H₁₂N₂, m.p. 264—265° (decomp.); these results are in disagreement with those of Madelung and Tencer (A., 1915, i, 719). Thionaphthen and S (80 hr. at 230—240°) afford the substances, C₁₆H₈S₃, m.p. 190—193°, and (C₁₆H₈S₃)_n, m.p. 292—293°. R. T.



(I.)

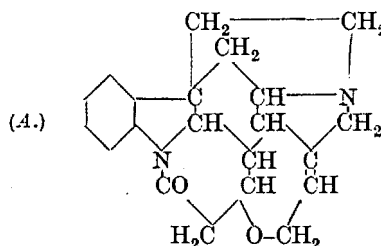
Nomenclature of heteroacyclic and heterocyclic compounds. G. KRAVTSOFF (Bull. Soc. chim., 1939, [v], 6, 581—586).—The application to heteroacyclic compounds of nomenclature previously proposed for heterocyclic compounds is discussed.

A. L.

Alkaloids of Papaver types. III. Alkaloids of *Roemeria refracta*, D.C. R. KONOVALOVA, S. JUNOUSSON, and A. OREKHOV (Bull. Soc. chim., 1939, [v], 6, 811—817; cf. A., 1936, 88, 217).—The C₂H₂Cl₂ extract of the plant, moistened with aq. NH₃, and treated with HCl, affords an alkaloid, roemerine (I), C₁₆H₁₂NMe(O₂CH₂), m.p. 102—103°, [α]_D²⁰ -77.18° in EtOH (hydrochloride, m.p. 262—263°; picrate, m.p. 195—196°). Its methiodide, m.p. 215—216°, and KOH-MeOH on bath (100°) give 6-dimethylaminomethylenedioxyphenanthrene, m.p. 73—74°. The methiodide, m.p. 274—275°, of the latter and KOH-MeOH gives NMe₃ and methylenedioxy-6-ethenylphenanthrene, m.p. 86—87°, oxidised by KMnO₄-COMe₂ to the methylenedioxy-phenanthrene-6-carboxylic acid, m.p. 263—264°, decarboxylated (quinoline-Cu chromite catalyst) to the phenanthrene, m.p. 84—85° (picrate, m.p. 167—168°). A. T. P.

Alkaloids of fumariaceous plants. XIX. *Corydalis ophiocarpa*, Hook. f. et Thoms. XX. *Corydalis micrantha* (Engelm.), Gray, and *Corydalis crystallina*, Engelm. R. F. MANSKE (Canad. J. Res., 1939, 17, B, 51—56, 57—60; cf. A., 1939, III, 190).—XIX. The following have been isolated: berberine, l-canadine, l-corypalmine, l-adlumine, protopine, α-alloeryptopine, cryptocavine, ophiocarpine (I), C₂₀H₂₁O₅N (F. 39), m.p. 188°, [α]_D²⁰ -284° in CHCl₃ (methiodide, m.p. 271°), and an alkaloid F. 40, m.p. 196°. (I) is probably 13-hydroxycanadine. XX. Protopine, l-tetrahydropalmatine, capaurine, capauridine, scoulerine, and three phenolic alkaloids, F. 41, m.p. 177°, F. 42, m.p. 239°, and F. 43, m.p. 230°, have been obtained from *C. micrantha*. From *C. crystallina*, protopine, bicuculline, and capnoidine have been isolated. F. R. S.

Strychnine and brucine. XLI. Re-examination of the action of bromine on diketonucidine and its bearing on the structure of the alkaloids. H. L. HOLMES and (Sir) R. ROBINSON (J.C.S., 1939, 603—608).—The descriptive results of Leuchs (A., 1932, 953) for the action of Br on diketonucidine in aq. solution have been repeated but the product isolated is found to be diketonucidine perchlorate, and not a Br-base. The argument from this reaction is accordingly reversed and examination of other reasons for the belief that the β-position of the hydroindole nucleus bears a H atom throws serious doubt on the validity of this conclusion. The base C₁₇H₂₀O₃N₂Br, obtained from cactotheline by the action of Br (Leuchs *et al.*, A., 1922, i, 1052), is probably 3:3-dibromo-2-hydroxynucine, and its product



(A.)

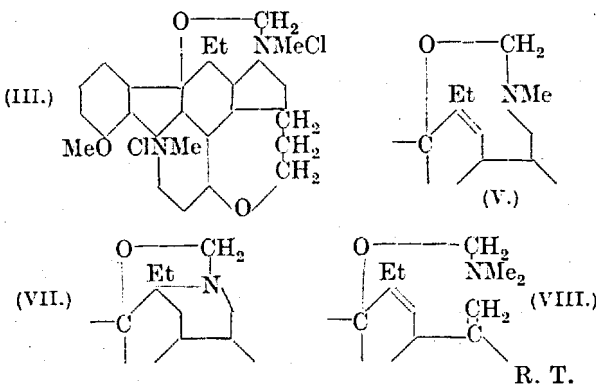
of hydrolysis, C₁₇H₂₂O₅N₂, 2-keto-3-hydroxynucine hydrate. The balance of evidence points to strychnine being (A). F. R. S.

Strychnos alkaloids. CV. Action of bromine water on 2:3-diketonnucidine. H. LEUCHS and H. GRUNOW (Ber., 1939, 72, [B], 679—684).—Gradual addition of 0.4N-Br-H₂O to 2:3-diketonnucidine in H₂O gives the bromohydrin (I), C₁₇H₂₁O₄N₂Br, [α]_D²⁰ +99.8°/d in abs. EtOH, which gives a black resin at ~190°. (I) gives a perchlorate, a semicarbazone, and a methiodide but does not afford a cryst. Ac derivative. Hydrogenation (PtO₂ in H₂O) of (I) leads to 2-keto-3-hydroxydihydro-oxynucidine (II), C₁₇H₂₄O₄N₂, isolated as the perchlorate (II), [α]_D²⁰ +57.6°/d in H₂O. Aq. Ba(OH)₂ and (I) at 95° afford the base, C₁₇H₂₀O₄N₂, m.p. ~232° after softening and darkening, [α]_D²⁰ -29.3°/d in EtOH (perchlorate, [α]_D²⁰ +133.9°/d in H₂O; methiodide; semicarbazone, [α]_D²⁰ +161°/d), hydrogenated (PtO₂) to (I). (II) is converted by Ac₂O and NaOAc at 95° into a non-cryst. Ac₂ derivative, isolated as the methiodide, C₂₁H₂₃O₆N₂MeI, m.p. ~285° (decomp.). (I) and boiling aq. Ba(OH)₂ yield the hydrate, C₁₇H₂₂O₅N₂, isolated as the perchlorate, [α]_D²⁰ -31°/d, also formed by the action of boiling aq. Ba(OH)₂ on C₁₇H₂₀O₄N₂. Diketonnucidine methoperchlorate reacts with considerable difficulty and at a higher temp. with Br-H₂O and the product when fractionated yields the Br-free salt, C₁₇H₂₂O₅N₂HClO₄ which contains 2 OH either formed directly or by the hydrolysis of an intermediate bromohydrin. Br therefore does not substitute an assumed :N-CO-CO-CH group in diketonnucidine but oxidises its C:C linking to a bromohydrin. H. W.

Chemical constitution of strychnine. IX. ψ-Strychnine and its derivatives. M. KOTAKE,

T. SAKAN, and S. KUSUMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 35, 415—418; cf. A., 1937, II, 312).—Strychnine (I) and O_3 in $CHCl_3-C_6H_6$ at 0° give ψ -strychnine (II), which gives 3% of β -indolyethylamine. When melted with KOH, *N*-methylchano- ψ -strychnine (III) gives *N*-methyltryptamine. The absorption spectra of (II) and (III) are similar, but differ from that of (I). The presence of (A) in (I) is thus indicated.

Structure of vomicine. Exhaustive methylation of dihydrovomicine. O. ACHMATOVICZ and B. RACINSKI (Rocz. Chem., 1938, 18, 315—335).—The dimethocarbonate, m.p. 200° (decomp.), of dihydrovomicine (I) heated at 230° yields *O*-methyl-dihydrovomidine-A (II), m.p. $216.5-217^\circ$ [methiodide, m.p. $211-212^\circ$ (decomp.); methochloride, m.p. $207-208^\circ$; dimethiodide, m.p. $207-208^\circ$ (decomp.)]; dimethochloride (III), m.p. $196-198^\circ$; dimethocarbonate (IV), m.p. $160-165^\circ$ (decomp.), also obtained by heating the hydrochloride, m.p. $178-183^\circ$ (decomp.), of (I) with KOH-MeOH at 135° , or by catalytic hydrogenation (Adams' Pt catalyst) of *O*-methylvomidine. (IV) heated at 230° , or (III) heated with KOH-MeOH at 150° , yields *O*-methyl-*N*₅-methyl-desdihydrovomidine (V), m.p. $191-192^\circ$ [methiodide, m.p. $196-198^\circ$ (decomp.); methochloride, m.p. $127-132^\circ$; methocarbonate, m.p. $140-145^\circ$ (decomp.); dimethochloride, m.p. $185-187^\circ$; dimethocarbonate (VI), m.p. $176-178^\circ$ (decomp.)]. (V) and boiling 20% H_2SO_4 yield (II) and *O*-methyl-dihydrovomidine-D (VII), m.p. $198-200^\circ$ [methiodide, $+2H_2O$, m.p. $195-196^\circ$ (decomp.); methochloride, m.p. $219-221^\circ$], also obtained by catalytic hydrogenation of (V) in 10% HCl. (VI) heated at 230° yields (V) and *O*-methyl-*N*₅-*N*₆-dimethyl-desvomidine (VIII), m.p. $245-246^\circ$ (decomp.), hydrogenated (Pt catalyst) at room temp. to dihydro-*O*-methyl-*N*₅-*N*₆-dimethyl-desvomidine, m.p. $140-141^\circ$ (dimethiodide, m.p. $249-250^\circ$), and at 70° to tetrahydro-*O*-methyl-*N*₅-*N*₆-dimethyl-desvomidine, an oil (methiodide, m.p. $175-178^\circ$). The following formulæ are proposed:



pounds. J. CHATT and F. G. MAXN (J.C.S., 1939, 610—615).—*o*-Phenylenediarsine tetrachloride, (+2 dioxan), m.p. 76—86°, prepared from the corresponding oxychloride and SOCl_2 , with the appropriate Grignard reagent gives *o*-phenylenebis(dimethylarsine), b.p. 156°/20 mm. and *-(di-n-butylarsine)*, b.p. 245—247°/20 mm. Ethylene- $\alpha\beta$ -bis(phenylarsinic acid) (improved prep.) with HCl-KI-SO_2 affords ethylene- $\alpha\beta$ -bis(phenylchloroarsine), m.p. 91—93° (corresponding *-iodo*-compound, m.p. 82°), which with MgPhBr yields ethylene- $\alpha\beta$ -bis(diphenylarsine), m.p. 99—102°, and with MgBuBr gives the *-(phenyl-n-butylarsine)*, b.p. 184—188°/0.06 mm. The latter compound with MeI and Na picrate gives β -, m.p. 139.5—140.5°, and α -forms, m.p. 113—115°, of ethylene- $\alpha\beta$ -bis(phenylmethyl-n-butylarsonium picrate). The arsine and Br followed by H_2S give β -, m.p. 120.5—121.5° (additive product, $3\text{C}_{22}\text{H}_{39}\text{S}_2\text{As}_2\text{C}_6\text{H}_{12}$, m.p. 114°), and α -forms, m.p. 113—116° (additive product, $6\text{C}_{22}\text{H}_{39}\text{S}_2\text{As}_2\text{C}_6\text{H}_{12}$, m.p. 87—89°), of ethylene- $\alpha\beta$ -bis(phenyl-n-butylarsine sulphide); the α - is converted into the β -sulphide by heating at 110°. The α - and β -forms of the two compounds are probably *meso*- and *racemic* forms, since they contain two asymmetric 4-covalent As atoms.

F. R. S.

Synthesis of organic compounds of bismuth.

L. A. SHITKOVA, N. I. SCHEVERDINA, and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 1839—1843).— BiCl_3 and Mg mesityl bromide in Et_2O give trimesitylbismuthine, m.p. 136—137° (dichloride, decomp. at 150°; dibromide, not melting at 250°). BiCl_3 and MgPhCl in PhMe (6 hr. at the b.p.) yield BiPh_3 , a CCl_4 solution of which reacts with $\text{Pb}(\text{OAc})_4$ to give $\text{BiPh}_3(\text{OAc})_2$.

R. T.

Organic derivatives of boron. II. Analysis of arylboric acids. N. N. MELNIKOV. III. Synthesis of aryl- and diaryl-boric acids. N. N. MELNIKOV and M. S. ROKITZKAJA (J. Gen. Chem. Russ., 1938, 8, 1766—1767, 1768—1775).—II. Excess of 0.1N- Br in KBr is added to 0.05—0.2 g. of arylboric acid in 50—150 ml. of H_2O at 0°, 5—10 ml. of 5% KI and 3 ml. of 5% HCl are added after 2 hr., and the solution is titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$. The B content is calc. according to the equations: $\text{BR}(\text{OH})_2 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{RBr} + \text{HBr} + \text{H}_3\text{BO}_3$; $\text{BR}_2\cdot\text{OH} + 2\text{Br}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{RBr} + 2\text{HBr} + \text{H}_3\text{BO}_3$.

III. 1 : 4 : 2- $\text{C}_6\text{H}_3\text{MeClBr}$ is added to Mg in Et_2O , and the solution is added to $\text{B}(\text{OH})_3\cdot\text{O}^n\text{Bu}^n$ in Et_2O ; 5-chloro-2-methylphenyl-, m.p. 184—186°, and 5 : 5'-dichloro-2 : 2'-dimethyldiphenyl-boric acid, m.p. 81°, are thus obtained. The following are prepared analogously: 2-bromo-4-methyl-, m.p. 157°, from 1 : 3 : 4- $\text{C}_6\text{H}_3\text{MeBr}_2$, *p*-ethylphenyl-, m.p. 108—111°, from *p*- $\text{C}_6\text{H}_4\text{EtBr}$, styryl-, m.p. 138—141°, from $\text{CHPh}\cdot\text{CHBr}$, diphenyl-, m.p. 185—190°, and *bis*-diphenyl-, not melting at 300°, from $\text{C}_6\text{H}_5\text{PhBr}$, 5-bromo-2 : 4-dimethylphenyl-, m.p. 206—211°, from dibromo-*m*-xylene, 5-chloro-2 : 4-dimethylphenyl-, m.p. 155—157°, from chlorobromo-*m*-xylene, 5-chloro-4-methylphenyl-, m.p. 242—247°, from 1 : 2 : 4- $\text{C}_6\text{H}_3\text{MeClBr}$, 4 : 4'-dichlorodiphenyl-, m.p. 75°, from *p*- $\text{C}_6\text{H}_4\text{ClBr}$, and 4-chlorobenzyl-boric acid, m.p. 140°, from *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Br}$. The arylboric acids, $\text{BR}(\text{OH})_2$, heated with Ti^{III} halides in H_2O , yield TiR_2X , HX , and

H_3BO_3 ($\text{R} = 5\text{-bromo-2 : 4-dimethylphenyl-}$, $\text{X} = \text{Cl}$, decomp. 268°, $\text{X} = \text{Br}$, decomp. 220°; $\text{R} = 5\text{-chloro-2 : 4-dimethylphenyl-}$, $\text{X} = \text{Cl}$, decomp. 248°, $\text{X} = \text{Br}$, decomp. 190—195°; $\text{R} = 5\text{-chloro-2-methylphenyl-}$, $\text{X} = \text{Cl}$, decomp. 260°, $\text{X} = \text{Br}$, decomp. 290°; $\text{R} = 5\text{-chloro-2-methylphenyl-}$, $\text{X} = \text{Cl}$, m.p. 211°, $\text{X} = \text{Br}$, m.p. 156°; $\text{R} = 2\text{-bromo-4-methylphenyl-}$, $\text{X} = \text{Cl}$, m.p. 238°, $\text{X} = \text{Br}$, m.p. 253°; $\text{R} = p\text{-ethylphenyl-}$, $\text{X} = \text{Cl}$, decomp. 260°, $\text{X} = \text{Br}$, decomp. 280°; $\text{R} = xylyl\text{-}$, $\text{X} = \text{Br}$, m.p. 196°). The compounds TiR_2X heated with aq. TiX_3 yield TiR_2X_2 ($\text{R} = 2\text{-bromo-4-methylphenyl-}$, $\text{X} = \text{Cl}$, m.p. 174—177°; $\text{R} = p\text{-ethylphenyl-}$, $\text{X} = \text{Cl}$, decomp. 155°; $\text{R} = \alpha\text{-naphthyl-}$, $\text{X} = \text{Cl}$, m.p. 144°; $\text{R} = 5\text{-bromo-}$, m.p. 192°, or 5-chloro-2 : 4-dimethylphenyl-, $\text{X} = \text{Br}$, m.p. 185—190°; $\text{R} = 5\text{-chloro-4-methylphenyl-}$, $\text{X} = \text{Br}$, m.p. 185—188°).

R. T.

Decomposition of mercury diphenyl in alcohols. M. M. KOTON (J. Gen. Chem. Russ., 1938, 8, 1791—1796).— HgPh_2 , heated at 200° with alcohols, yields Hg , C_6H_6 , aldehyde, and ester: $\text{HgPh}_2 \rightarrow 2\text{Ph}' + \text{Hg}$; $2\text{Ph}' + \text{R}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{R}\cdot\text{CHO} + 2\text{C}_6\text{H}_6$; $2\text{R}\cdot\text{CHO} \rightarrow \text{R}\cdot\text{CO}_2\cdot\text{CH}_2\text{R}$. The velocity of the reaction falls in the series $\text{R} = \text{H} > \text{Bu}^t > \text{Ph} > \text{Et} > \text{Me} > \text{Pr}^i > \text{Pr}^n$, and for poly- > mono-hydric alcohols (glycol > mannitol > glycerol).

R. T.

Reaction of powdered metals or metalloids with lithium phenyl or magnesium phenyl bromide. Reaction of lithium with the phenyl compounds of metals of groups II, IV, and V of the periodic system. T. V. TALALAEVA and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 1831—1838).—The reactions $2\text{LiPh} + \text{M} \rightarrow \text{MPh}_2 + 2\text{Li}$ ($\text{M} = \text{Mg}$, Hg); $3\text{LiPh} + \text{M} \rightarrow \text{MPh}_3 + 3\text{Li}$ ($\text{M} = \text{As}$, Sb); $4\text{LiPh} + \text{M} \rightarrow \text{MPh}_4 + 4\text{Li}$ ($\text{M} = \text{Sn}$, Pb), take place in boiling xylene solution. With Bi and Si , LiPh yields Ph_2 , but not organometallic compounds. The reverse reactions take place (with difficulty) in the cases of HgPh_2 , PbPh_4 , and BiPh_3 , but not of SiPh_4 , SnPh_4 , AsPh_3 , or SbPh_3 . MgPhBr in Et_2O and As (25 hr. at the b.p.) yield AsPh_3 ; analogous reactions are not observed with Pb , Sn , or Sb .

R. T.

Metallation of cyclic compounds. R. L. BEBB (Iowa State Coll. J. Sci., 1938, 13, 41—43; cf. Gilman and Young, A., 1934, 899).—Dibenzthiophen with LiBu^t in Bu_2O at 80°/20 hr. followed by treatment with CO_2 affords dibenzthiophen-4-carboxylic acid (90%); with Na *n*-amyl the yield is 37%. $(\text{CH}_2\text{Ph})_2$ with NaBu^t in NBU^t_3 or KBu^t in C_6H_6 , followed by CO_2 , similarly affords $(\text{CHPh}\cdot\text{CO}_2\text{H})_2$ (30% and 52%, respectively). With LiBu^t 0.1% of *p*- β -phenylethylbenzoic acid is formed. Similarly $\text{CH}_2\text{Ph}\cdot\text{C}_8\text{H}_4\text{Me-p}$, $\text{CH}_2\text{Ph}\cdot\text{C}_{10}\text{H}_7\text{-1}$, and 9 : 10-dihydroanthracene with LiBu^t afford phenyl-*p*-tolyl- (49%) and phenyl-1-naphthyl-acetic acid (80%), and 9 : 10-dihydroanthracene-9-carboxylic acid (80%) (8% of the -9 : 10-dicarboxylic acid is also formed), respectively. Ph_2 with LiBu^t in Et_2O gives a mixture (7—15%) of *o*- and *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$ but there is no reaction in C_6H_6 or light petroleum. C_{10}H_8 with LiBu^t for 30 hr. gives a mixture (20%) of α - and β - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$; the yield is 28% with NaBu^t in boiling NBU^t_3 for 36 hr. Phenanthrene does not react with

LiBu^a but furan and 2-methylfuran with LiPh afford furoic (38%) and 5-methyl-2-furoic acid (17%), respectively. 2:5-Dimethylfuran yields an unstable acid. 2-Methoxydibenzfuran with LiBu^a similarly affords 2-methoxydibenzfuran-1- (40%) and -3-carboxylic acid (20%). PhOMe with LiBu^a similarly yields *o*-OMe·C₆H₄·CO₂H (19%) and di-*o*-anisyl ketone (40%); with NaPh in C₆H₆ for 48 hr., the yield of the acid is 64%. Ph₂O and Ph₂S with LiBu^a afford *o*-OPh·C₆H₄·CO₂H and *o*-SPh·C₆H₄·CO₂H (and some PhSH), respectively. Similarly treated, Ph₂Se affords SePhBu^a and BzOH. CNa:CH in liquid NH₃ with Δ^a-heptinene and CPh:CH affords Na Δ^a-heptinenyl and Na phenylethynyl, respectively J. L. D.

Selenium aryl halides. VII. Organic selenide dihalides. O. BEHAGEL and K. HOFMANN (Ber., 1939, 72, [B], 697—712).—(CH₂Ph)₂Se₂ in MeOH is transformed by 25% KOH-EtOH and EtBr into CH₂Ph Et selenide, b.p. 111—113°/14 mm., which with Br in well-cooled CHCl₃ decomposes into SeEtBr₃, m.p. 74°, CH₂Ph being less firmly retained than Et to Se. Ph CH₂Ph selenide, b.p. 200—202°/15 mm., obtained analogously, gives immediately CH₂PhBr and SePhBr in spite of careful cooling. 2:2'-Dinitrodiphenyl diselenide and CH₂PhCl afford *o*-nitrophenyl CH₂Ph selenide, m.p. 100°, transformed by Br into CH₂PhBr and Se *o*-nitrophenyl bromide, m.p. 64°, and by excess of Cl₂ in CHCl₃ into Se *o*-nitrophenyl trichloride, m.p. 154°. *o*-Nitrodiphenyl selenide is converted by Cl₂ in CHCl₃ into Se *o*-nitrodiphenyl dichloride, NO₂·C₆H₄·SePhCl₂, m.p. 170—171°, and by Br in CHCl₃ into the corresponding dibromide (I), m.p. 108°, either of which can be cautiously hydrolysed to Se *o*-nitrodiphenyl oxide, m.p. 137—138°. 2:1:4-NO₂·C₆H₃Br·NH₂ is converted by PhSeH and KOH-EtOH in boiling MeOH into 2-nitro-4-aminodiphenyl selenide, m.p. 89—90°, the hydrobromide of which is transformed by diazotisation and treatment with CuBr into 4-bromo-2-nitrodiphenyl selenide, m.p. 119—120°, identical with the product of the decomp. of (I), showing thus that Br has entered *p*- to Se and *m*- to NO₂ in the nucleus. SePhBr and *p*-C₆H₄Me·MgBr in well-cooled Et₂O afford Ph *p*-tolyl selenide, b.p. 186°/14 mm., smoothly converted into the corresponding dichloride, m.p. 126—127°, and dibromide (II), m.p. 137—138°. SePhCl₂, AlCl₃, and Ph₂ afford (non-homogeneous) Ph₂ *p*-diphenyl selenonium chloride, m.p. 130—135° (decomp.), which passes at 130° into PhCl and Ph 4-diphenyl selenide, m.p. 66—67°; this yields a dichloride, m.p. 201°, and a dibromide (III), m.p. 161—162°, either of which is hydrolysed by 2N-Na₂CO₃ to the oxide, m.p. 134—135°. 2:4'-Dimethyldiphenyl selenide, b.p. 196°/14 mm., from *p*-C₆H₄Me·MgBr and *o*-C₆H₄Me·SeBr, yields a dibromide (IV), m.p. 171°, hydrolysed to the corresponding oxide, m.p. 136—138°. Impure 3:4:4'-trimethyldiphenyl selenide, b.p. 201—203°/15 mm., gives a dibromide (V), m.p. 161—162°, and oxide, m.p. 69—70°. Se(C₆H₄Me)₂Cl₂ and Ph₂ afford Se *di-p*-tolyl 4-diphenyl chloride, which passes when distilled into *p*-tolyl 4-diphenyl selenide, m.p. 98—99°; this affords a dibromide (VI), m.p. 146—148°, and an oxide, m.p. 137—138°. 2-Aminodiphenyl hydrochloride is diazotised and converted by K₂Se into

2:2'-didiphenyl selenide, m.p. 128—129°, which gives a dichloride, m.p. 143—144°, and dibromide, m.p. 124—125°; these are hydrolysed by cautious warming with dil. Na₂CO₃ into the oxide, m.p. 142°, from which the di-iodide, m.p. 104—106°, is obtained by trituration with HI. 4-Aminodiphenyl hydrochloride is transformed similarly into a mixture which when heated to 250° gives Se and 4:4'-didiphenyl selenide, m.p. 151—152° [dibromide (VII), m.p. 203—205°]. 2:4-NO₂·C₆H₃Br·NH₂ when diazotised and treated with KCNSe yields 4-bromo-2-nitrophenyl selenocyanide, m.p. 141°, transformed by NaOEt in EtOH into 4:4'-dibromo-2:2'-dinitrodiphenyl diselenide, m.p. 178°, which even with an excess of Br in CHCl₃ affords solely Se 4-bromo-2-nitrophenyl bromide, m.p. 116°. Diphenylene selenide yields the dichloride (VIII), m.p. 136—137°, dibromide (IX), m.p. 129°, and oxide, m.p. 219—221°. SePhEtBr₂ when heated at about 10—20° above its m.p. yields SePhBr and EtBr. (II) gives a nucleus-brominated Ph *p*-tolyl selenide, C₁₃H₁₁BrSe, m.p. 64—65°. Similarly a brominated Ph *p*-diphenyl selenide is obtained from (III). In a similar manner (IV), (V), (VI), and (VII) give compounds, C₁₄H₁₃BrSe, m.p. 86—88°, C₁₅H₁₅BrSe, m.p. 76—78°, C₁₆H₁₇BrSe, m.p. 79—80°, and C₂₄H₁₈BrSe, m.p. 161°. 3-Chlorodiphenylene selenide, identified as its dibromide, m.p. 130—131°, is derived from (VIII), and a bromodiphenylene selenide, m.p. 95°, results from (IX). H. W.

Study of the action of hydrogen chloride on aromatic tin organic compounds of the type SnAr'₂Ar''₂, with the object of establishing a series of relative electronegativity of certain radicals. T. S. BOBASCHINSKAJA and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 1850—1856).—Compounds SnR₂R'₂ with HCl in H₂O or C₆H₆ give SnR₂Cl₂ and R'H (R = cyclohexyl, R' = Ph; R = Ph, R' = *p*-anisyl, m.p. 125—126°; R = α-C₁₀H₇, R' = *p*-anisyl, m.p. 186—187°; R = Ph, R' = α-C₁₀H₇, m.p. 209—210°; R = Ph, R' = α-thienyl, m.p. 202—210°; R = α-C₁₀H₇, R' = α-thienyl, m.p. 145—146°; R = *p*-anisyl, R' = α-thienyl, m.p. 89—93°). On this basis the following series of radicals, in order of increasing electronegativity, is given: cyclohexyl, Ph, α-C₁₀H₇, *p*-anisyl, α-thienyl. R. T.

Tin organic compounds of the naphthalene series. E. I. PIKINA, T. V. TALALAEVA, and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1938, 8, 1844—1849).—α-C₁₀H₇·MgBr in Et₂O-C₆H₆ and SnCl₄ yield a tarry product, which reacts with SnCl₄ in xylene (3 hr. at 150°) to give (α-C₁₀H₇)₂SnCl₂. This with NH₃ in aq. EtOH gives di-α-naphthylstannone, with KSH in aq. EtOH gives di-α-naphthylstannithione, m.p. 215°, with Br in CHCl₃, or with KI in COMe₂ yields di-α-naphthyl-dibromo-, m.p. 142°, or di-iodo-stannane, m.p. 160°, with SnCl₄ affords α-naphthyltrichlorostannane, m.p. 77—78°, with HgCl₂ in EtOH gives α-C₁₀H₇·HgCl, and with MgPhBr in Et₂O gives SnPh₃·C₁₀H₇-α. R. T.

Structure of proteins. (A) W. T. ASTBURY and (Miss) F. O. BELL. (B) I. LANGMUIR (Nature, 1939, 143, 280).—A criticism and a reply. L. S. T.

Chemical aspects of the cyclol hypothesis. A. NEUBERGER (Nature, 1939, 143, 473).—The cyclol theory does not explain denaturation. Other evidence, claimed to support the theory, is criticised.

L. S. T.

Structure of the globular proteins. D. WRINCH (Nature, 1939, 143, 482—483).—Recent objections to the cyclol theory are summarised and replies made to them.

L. S. T.

Structure of proteins. D. M. WRINCH (Proc. Roy. Inst., 1939, 30, 541—557).—A lecture.

"Intraglobular" reactions and the cyclol structure of proteins.—See A., 1939, I, 320.

Heavy oxygen exchange reactions of proteins and amino-acids.—See A., 1939, I, 333.

Analysis of proteins. XI. Products of action of sodium hydroxide on caseinogen. Composition of dephosphocasein (depocasein). R. H. A. PLIMMER and J. H. T. LAWTON (Biochem. J., 1939, 33, 530—542).—1% NaOH on caseinogen at 37° removes P and gives a substance containing 55% of the original N and resembling a metaprotein in its solubility in 0.1N-acid or -alkali. The tyrosine content is 1% > that of caseinogen, whilst methionine, lysine, and proline are somewhat lower. Glutamic acid (3.6) is \ll in caseinogen (21.0%).

P. G. M.

Thiol groups in proteins. II. Edestin, excelsin, and globin in solutions of guanidine hydrochloride, carbamide, and their derivatives. J. P. GREENSTEIN (J. Biol. Chem., 1939, 128, 233—240; cf. A., 1938, II, 517).—Solutions of edestin, excelsin, and globin (but not amandin) in aq. guanidine hydrochloride or (to a smaller extent) *N*-methylguanidine or $\text{CO}(\text{NH}_2)_2$ contain SH groups corresponding with 0.1—0.5% of cysteine. This proportion is independent of protein concn., and bears no direct relation to the mol. wt. of the proteins in these solutions; its relation to the amount of alkali-labile S in each protein is discussed. NH_2Ac , $\text{NH}_2\text{CO-NHMe}$, and *NN*-dimethylguanidine have no such effect.

A. LI.

Sericin. III—V.—See A., 1939, III, 488, 597.

Non-hydrolytic degradation products of fibrin. Action of proteinases on them. J. FEIGENBAUM (Enzymologia, 1939, 6, 122—134).—Fibrin, heated (3 hr.; 135—145°) in $\beta\text{-C}_{10}\text{H}_7\text{-OH}$, yields acropeptides (I) (mol. wt. 690—923), separated by treatment with abs. and dil. EtOH and pptn. with Et_2O . Leucine, proline, glutamic and aspartic acid, alanine, lysine, histidine, and arginine are constituents of the (I), which are closed-chain octapeptides or associations of such octapeptides. The (I) are attacked by pepsin and papain and, after (but not before) treatment with pepsin and/or papain, by yeast-polypeptidase. The structure of fibrin probably does not differ much from that of non-fibrous proteins.

W. McC.

Spectrophotometric study of the biuret reaction in investigations into the structure of proteins. I. N. I. GAVRILOV, A. I. PARADACHVILI, and A. I. GOVOROV (Enzymologia, 1939, 6,

94—104; cf. Kober and Haw, A., 1916, i, 377).—Spectrophotometric examination of the colours produced on applying the biuret test to the products of hydrolysis of caseinogen and serum-albumin (ox) by pepsin, trypsin, and pancreatin shows that a relationship exists between the shade and intensity of the colour, the rate of production or disappearance of NH_2 groups, and the extent of hydrolysis or ring formation.

W. McC.

Separation of liquid mixtures by combined thermo-diffusion and thermo-siphon action.—See A., 1939, I, 282.

Determination of maltose in presence of other sugars. F. HOEKE (Chem. Weekblad, 1939, 36, 237—241).—Mixtures of maltose and glucose, fructose, invert sugar, or sucrose can be analysed by chemical methods which are not applicable when dextrans are present. In this case biochemical (fermentation) methods must be used. *Torulopsis dattila* (Kluyver), Lodder, slowly attacks maltose under aerobic conditions but *T. utilis* (Henneberg), Lodder, has practically no action. The maltose content of mixtures containing glucose and dextrans can be determined satisfactorily by fermentation with *T. utilis* and *Saccharomyces cerevisiae*.

S. C.

Determination of cholesterol by oxidation with chromic acid. F. KAYSER and C. MATHIEU (Bull. Soc. chim., 1939, [v], 6, 715—717).—Cholesterol digitonide is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ in boiling aq. H_2SO_4 with a little 25% aq. AgNO_3 (catalyst) for 40 min.; Ag is removed by aq. NaCl, the mixture filtered, and excess of $\text{K}_2\text{Cr}_2\text{O}_7$ determined iodometrically (cf. Okey, A., 1930, 1303; Yasuda, A., 1931, 1318).

A. T. P.

Micro-detection of salicylic acid as silver salicylate. H. JURÁNY (Mikrochem., 1939, 26, 314—318).—The substance is dissolved in a min. of 10% aq. NH_3 and a large drop of H_2O is added. After addition of a small drop of 3% aq. AgNO_3 the solution is allowed to evaporate spontaneously. The residue is washed with a drop of EtOH to remove the excess of AgNO_3 , when Ag salicylate remains in monoclinic prisms which may be identified by the crystal angles, oblique extinction, and the relation of these to the crystal outline. The method of distinguishing between Ag salicylate and AgOBz is described in detail. The limiting sensitivity of the method is 0.4 μg . of salicylic acid. The reaction may be applied to micro-sublimates. Cinnamic and phthalic acids interfere with the test.

J. W. S.

Determination of methylene-blue. G. GURMENDI and J. DE D. GUEVARA (Bol. Soc. Quím. Peru, 1938, 4, 283).—Pptn. with picric acid and iodometric titration both give satisfactory results.

F. R. G.

Semimicro- and micro-chemical study of genalkaloids (genstrychnine and genatropine). B. MENENDEZ (Rev. Fac. Cienc. Quím. La Plata, 1938, 13, 141—144).—The amounts of strychnine and atropine oxides which can be identified in micro-quantities are comparable with those for the respective alkaloids.

F. R. G.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1939.

Conception of mesomerism in organic chemistry. B. EISTER (Angew. Chem., 1939, 52, 353—361).—Mesomerism, the displacement of π electrons in systems with multiple linkings from the defined extreme positions into an intermediate arrangement which cannot be symbolised in the usual manner, is a phenomenon necessitated by much experiment and explained fundamentally. The electron theory enables this intermediate state to be circumscribed by giving the limits within which the π electron cloud remains "suspended." For mesomerism, the method of writing limiting formulæ has the advantage that it gives definite information concerning the electron balance; usually these formulæ are also the reaction formulæ of mesomeric compounds. The following are the constitutional essentials so that two or more isomeric formulæ have mesomeric and not tautomeric relationships. There must be the same steric sequence of all actually united atoms (*i.e.*, they must not stand in ionic relationship) and only the distribution of the electrons must be different; all atoms concerned with electron displacements must be able to lie in a plane. The energy of a mesomeric system is less than that calc. for each of the limiting formulæ. The passage to a mesomeric "energy cavity" and the consequent gain in energy is frequently the driving force for reactions in systems with multiple linkings. The quantum theoretical foundation for mesomerism and for its representation by limiting formulæ is given by regarding the total function of the π electron cloud approx. as "resonance" between the functions proper to the limiting formulæ. H. W.

Kinetics of cracking of normal paraffin hydrocarbons under pressure.—See A., 1939, I, 375.

Vapour-phase nitration of isopentane [β -methylbutane]. L. W. SEIGLE and H. B. HASS (Ind. Eng. Chem., 1939, 31, 648—650; cf. A., 1938, II, 79).— CHMe_2Et when nitrated at 380° or 420° gives COMe_2 , MeNO_2 (6:2), EtNO_2 (6:6), Pr^nNO_2 (6:11), Bu^nNO_2 + $\text{CHMeEt}\cdot\text{NO}_2$ (12:10), $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{NO}_2$ (11:28), $\text{CMe}_2\text{Et}\cdot\text{NO}_2$ (19:14), $\text{CH}_2\text{Bu}^n\cdot\text{NO}_2$ (13:13), and $\text{CHMePr}^n\cdot\text{NO}_2$ (27:16%). A. T. P.

Isomerisation of n -octane. A. P. MESCHTSCHERIAKOV and E. P. KAPLAN (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1055—1060).— n -Octane with HCl and AlCl_3 or HBr and AlBr_3 at room temp. undergoes 15—40% isomerisation, the octane no. being increased by 16 after 140 hr. The product after 1 hr. at 408 — 418° under pressure in presence of MoS_3 has an octane no. 8 > that of n -octane; in the change from n -octane to methylheptane, or

from this to dimethylhexane, there is an increase of 30—40. A. LI.

$\beta\zeta$ -Dimethylheptane: its synthesis and comparison with an isononane from petroleum. J. D. WHITE, F. W. ROSE, jun., G. CALINGAERT, and H. SOROOS (J. Res. Nat. Bur. Stand., 1939, 22, 315—319).— $\beta\zeta$ -Dimethylheptan- δ -ol hydrogenated (Calingaert and Soroos, A., 1936, 107) gives $\beta\zeta$ -dimethylheptane of 99.6% purity, the properties of which, extrapolated to 100% (b.p. $135.21 \pm 0.02^\circ$, f.p. $-102.95 \pm 0.10^\circ$, etc.), agree with the vals. for an isononane from petroleum (B., 1937, 314). F. R. G.

Cracking of hexadecane under pressure. A. D. PETROV and M. A. TSCHELTZOVA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1033—1037).—Cracking of $\text{C}_{16}\text{H}_{34}$ at 440 — 460° under pressure is accompanied by considerable isomerisation of the products. In presence of H_3PO_4 , the isomerisation and the yield of gas, unsaturated hydrocarbons, and liquid boiling above 200° are increased. A. LI.

Polymerisation of ethylene, propene, and Δ^2 -butene in still discharges. D. N. ANDREEV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1039—1053).—With the gas flowing at 18—20 l. per hr., the chief products are unsaturated aliphatic hydrocarbons, with considerable quantities of the dimeride of the original hydrocarbon. Of the product from C_3H_6 65%, from C_4H_8 46%, and from C_2H_4 29%, boils below 160° . A. LI.

Exchange reaction between ethylene and deuterium on a nickel catalyst.—See A., 1939, I, 377.

Infra-red analysis applied to the exchange reaction between ethylene and deuterioethylene.—See A., 1939, I, 377.

Isomerisation phenomena accompanying the reduction of diolefinic and aromatic hydrocarbons by means of calcium-ammonia. B. A. KAZANSKI and N. F. GLUSCHNEV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1065—1072).—With Ca-NH_3 at 0° , ($\text{CMe}:\text{CH}_2$) $_2$, cyclopentadiene, $\text{CHPh}:\text{CH}_2$, $\text{CHPh}:\text{CHMe}$, $\text{CH}_2:\text{CMe}:[\text{CH}_2]_2\text{CMe}:\text{CH}_2$, and $\text{CH}_2\text{Ph}:\text{CH}:\text{CH}_2$ are reduced respectively to $\text{CMe}_2:\text{CMe}_2$, cyclopentene, 1-ethyl- and 1- n -propyl- Δ^1 -cyclohexene (I), ($\text{CH}:\text{CMe}_2$) $_2$, and (I). Non-conjugated systems undergo isomerisation to conjugated systems before reduction. A. LI.

Preparation of true acetylene hydrocarbons. D. BODROUX (Compt. rend., 1939, 208, 1022—1024).—The Na_1 derivative of NH_2Ph with $\alpha\alpha$ - or $\alpha\beta$ -dihalogeno-derivatives of saturated hydrocarbons in

Et_2O at room temp. affords a product decomposed by H_2O to the unsaturated hydrocarbon. $(\text{CH}_2\text{Cl})_2$, $(\text{CH}_2\text{Br})_2$, or CHMeCl_2 affords $\text{CH}:\text{CH}$; $\text{CHMeBr}\cdot\text{CH}_2\text{Br}$ gives $\text{CMe}:\text{CH}$ (cf. Bourguet, A., 1925, i, 770); heptylidene dichloride gives Δ^2 -heptinine; $\text{CHPhBr}\cdot\text{CH}_2\text{Br}$ gives $\text{CPh}:\text{CH}$. $\text{CHPh}:\text{CHBr}$ with NaNH_2 in Et_2O containing a small amount of NH_2Ph gives $\text{CPh}:\text{CH}$ in good yield. J. L. D.

Action of lithium on an optically active aliphatic chloride. D. S. TARBELL and M. WEISS (J. Amer. Chem. Soc., 1939, 61, 1203—1205).—*Li* α -methyl-*n*-heptyl (I) is best (56%) obtained from *n*- $\text{C}_6\text{H}_{13}\cdot\text{CHMeCl}$ (II) and *Li* (excess) in Et_2O at 0° ; treating the solution with CO_2 gives *dl-n*- $\text{C}_6\text{H}_{13}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, but the unaltered (I) is \rightarrow slightly racemised. Racemisation probably occurs during reaction of (I) with *Li* rather than during carbonation. Racemisation of unaltered CHPhMeCl by *Na* may be due to the exchange reaction: $\text{dl-NaCHPhMe} + \text{d-CHPhMeCl} \rightarrow \text{dl-NaCHPhMe} + \text{dl-CHPhMeCl}$. R. S. C.

Halogenation of optically active tert. carbinols. P. G. STEVENS and N. L. MCNIVEN (J. Amer. Chem. Soc., 1939, 61, 1295—1296).—With HCl in pentane at 25° , $\text{Bu}^t\cdot[\text{CH}_2]_2\cdot\text{CMeEt}\cdot\text{OH}$, b.p. $89.0^\circ/15$ mm., $[\alpha]_D^{25} -0.45^\circ$, gives a *tert.* chloride, b.p. $71.0^\circ/9$ mm., $[\alpha]_D^{25} -0.28^\circ$, but at -78° gives the enantiomeric chloride (impure), b.p. $69-70^\circ/8$ mm., $[\alpha]_D^{25} +0.17^\circ$. Reaction may thus take either of two courses (cf. Levene *et al.*, A., 1939, II, 155). R. S. C.

Retardation of chemical reactions. IX. Stabilisation of perchloroethylene [tetrachloroethylene] for medicinal purposes. K. C. BAILEY (J.C.S., 1939, 767—769; cf. B., 1938, 977).—Decomp. of C_2Cl_4 , catalysed by light, is inhibited by thymol (1:500,000), not quite so well by Et_2O , EtOH , $\text{CS}(\text{NH}_2)_2$, $\text{Na}_2\text{S}_2\text{O}_3$, or *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and by various other substances. An excess of solid $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{CS}(\text{NH}_2)_2$ is more efficient than a saturated solution, probably owing to replacement of the inhibitor in solution as it is destroyed. R. S. C.

Action of Raney nickel on alcohols. Probabilisation of a union of the catalyst with the hydrogen receptors. R. PAUL (Compt. rend., 1939, 208, 1319—1321).—Raney Ni with boiling primary and *sec.* alcohols forms aldehydes or ketones with evolution of H_2 ; part of the alcohol is reduced. Furfuryl and cinnamyl alcohol afford methylfuran and propenylbenzene, respectively, with the appropriate aldehydes, which react further (temp. $>90^\circ$) to form furan and $\text{CHPh}:\text{CH}_2$, respectively, and CO_2 . The ketones derived from *sec.* alcohols do not react with Raney Ni at 180° (cf. Palfray and Sabetay, A., 1939, II, 115). If the alcohol is slowly distilled with Raney Ni a much better yield of ketone results, probably because the catalyst-ketone union is continually broken down during the distillation. Thus $\text{CHMeEt}\cdot\text{OH}$, $\text{CHEtPr}\cdot\text{OH}$, β - and γ -hydroxyoctane, and Pr^tOH yield 90%, 80%, 95%, 95%, and 30%, respectively, of the corresponding ketones. If an ethylenic or acetylenic compound is added to an easily oxidisable alcohol and Raney Ni, dehydrogenation is much reduced or prevented. J. L. D.

Butane- $\beta\gamma$ -diol and its esters. L. DENIVELLE (Compt. rend., 1939, 208, 1024—1025).—Butane- $\beta\gamma$ -diol (I), m.p. 26° , b.p. $178^\circ/742$ mm., with H_3PO_4 , H_2SO_4 , P_2O_5 , or anhyd. ZnCl_2 gives COMeEt . Equimol. amounts of (I) and SOCl_2 in C_6H_6 containing $\text{C}_5\text{H}_5\text{N}$ (2 mols.) afford a neutral sulphoxide, b.p. $70-71^\circ/12$ mm., which when passed over CaCO_3 at 275° gives a mixture of $\beta\gamma$ -oxidobutane (II) and COMeEt . With kaolin at 575° , $\text{CH}_2:\text{CH}\cdot\text{CH}:\text{CH}_2$ (III) (8—10%; small amounts at 450°) is formed. The diacetate of (I) with kaolin at $350-575^\circ$ affords (III); with CaCO_3 at 225° , (II) and COMeEt are formed. J. L. D.

isoPropylideneglyceraldehyde. IV. Preparation of *d*(+)-isopropylideneglycerol. V. Synthesis of optically active glycerides from *d*(+)-isopropylideneglycerol. VI. Synthesis of the biological *l*(-)- α -glycerophosphoric acid. E. BAER and H. O. L. FISCHER (J. Biol. Chem., 1939, 128, 463—473, 475—489, 491—500; cf. A., 1936, 708).—IV. *d*(+)-isoPropylideneglycerol (I), b.p. $78.5-79^\circ/11$ mm., $[\alpha]_D^{20} +12.6^\circ$, $+10.8^\circ$ in C_6H_6 , -1.70° in H_2O , $+11.09^\circ$ in $\text{C}_5\text{H}_5\text{N}$, $+10.7^\circ$ in MeOH , is obtained by catalytic reduction (Ni) of isopropylidene-*d*-glyceraldehyde (improved prep. from *d*-mannitol). (I) with BzCl -quinoline gives the *Bz* derivative, b.p. $159-160.5^\circ/10.5$ mm., $[\alpha]_D^{25} +12.31^\circ$, and with MeI - Ag_2O gives the *Me* derivative, b.p. $43-44^\circ/10.5$ mm., $[\alpha]_D^{20} +20.14^\circ$, $+12.88^\circ$ in $\text{C}_5\text{H}_5\text{N}$.

V. Acylation of (I) in $\text{C}_5\text{H}_5\text{N}$ or quinoline gives the following derivatives: *Ac*, b.p. $85-86^\circ/10-11$ mm., $[\alpha]_D^{20} +3.24^\circ$; *lauryl* (II), b.p. $130-131^\circ/0.002$ mm., $[\alpha]_D^{20} +3.42^\circ$, $+1.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *palmityl* (III), m.p. $33-35^\circ$, $\alpha_D^{30} +4.38^\circ$, $[\alpha]_D +2.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *stearyl* (IV), m.p. 43.5° , $\alpha_D^{30} +3.0^\circ$, $[\alpha]_D +1.9^\circ$ in $\text{C}_5\text{H}_5\text{N}$. All have zero rotation in C_6H_6 . Acid hydrolysis of (II), (III), and (IV) gives respectively: *α -lauryl-* (V), m.p. $53-54^\circ$, $[\alpha]_D -3.76^\circ$ in $\text{C}_5\text{H}_5\text{N}$, *α -palmityl-* (VI), m.p. $71-72^\circ$, $[\alpha]_D -4.37^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and *α -stearyl-glycerol* (VII), m.p. $76-77^\circ$, $[\alpha]_D -3.58^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Glycerol α -*p*-toluenesulphonate (VIII), m.p. $63-64^\circ$, $[\alpha]_D -7.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and α -*p*-nitrobenzoate (IX), m.p. $88-89^\circ$, $[\alpha]_D -17.1^\circ$ in EtOH , are also described. These α -monoglycerides belong to the *l*-glyceraldehyde series. On keeping (1 year) (V), (VI), and (VII) show a fall in rotation due to migration of the acyl groups, (VIII) and (IX) being unchanged. Acylation of (V), (VI), (VII), and (IX) in $\text{C}_5\text{H}_5\text{N}$ or quinoline gives respectively: *glycerol α -laurate $\beta\gamma$ -distearate* (X), m.p. 48.5° , $\alpha_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, *α -palmitate $\beta\gamma$ -dilaurate* (XI), m.p. 44° , $\alpha_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$, *α -stearate $\beta\gamma$ -dipalmitate* (XII), m.p. 62.5° , $\alpha_D 0^\circ$ in $\text{C}_5\text{H}_5\text{N}$ or CHCl_3 , *$\beta\gamma$ -dibenzoate α -*p*-nitrobenzoate* (XIII), m.p. $87-88^\circ$, $[\alpha]_D -19.9^\circ$ in $\text{C}_2\text{H}_2\text{Cl}_4$. Although (X), (XI), and (XII) have zero rotation, they are not considered to be racemic, because (V), (VI), and (VII) are not racemised in $\text{C}_5\text{H}_5\text{N}$ and (XIII) is optically active. It is considered that natural triglycerides with zero rotation are not necessarily racemic.

VI. *l*(-)- α -Glycerophosphoric acid (XIV) (*Et*₂ ether of *Et*₂ ester, b.p. $100-100.5^\circ/0.13$ mm., $[\alpha]_D^{25} -5.31^\circ$, -5.76° in EtOH) is synthesised from (I) by the method of Fischer and Pfähler (A., 1920, i, 807) and is identical with the glycerophosphoric acid in phos-

phatides (Kasser *et al.*, A., 1926, 384) and that formed as an intermediate in alcoholic fermentation and glycolysis (Meyerhof *et al.*, A., 1933, 1080). (XIV) belongs to the *l*-glyceraldehyde series and therefore cannot arise biologically from the natural *d*-glyceraldehyde-3-phosphoric acid, but must be formed by asymmetrical fermentative reduction from dihydroxy-acetonephosphoric acid. S. H. H.

Thermal decomposition of diethyl ether.—See A., 1939, I, 375.

Mechanism of hydrolysis of carboxylic esters and of esterification of carboxylic acids. Acid hydrolysis of an ester with heavy oxygen as isotopic indicator. S. C. DATTA, J. N. E. DAY, and C. K. INGOLD (J.C.S., 1939, 838–840).—During hydrolysis of Me H succinate by HCl in H₂O containing H₂¹⁸O, the ¹⁸O enters the acid, thus confirming the accepted mechanism. The fundamental mechanism of hydrolysis of esters in acid, neutral, and alkaline solutions, and the evidence in favour thereof, are reported. R. S. C.

Ancillary mechanisms in the hydrolysis and esterification of carboxylic esters. E. D. HUGHES, C. K. INGOLD, and S. MASTERMAN (J.C.S., 1939, 840–842).—Esterification of *n*-C₆H₁₃-CHMe-OH by AcOH in H₂O occurs without racemisation, but in dil. H₂SO₄ there is slight racemisation. The reaction mechanisms are discussed. R. S. C.

Compressed catalysts [for preparation of ethyl acetate from ethyl alcohol].—See A., 1939, I, 377.

Polymerisation of vinyl acetate.—See A., 1939, I, 377.

Action of sodium on fatty acid chlorides of higher mol. wt. A. W. RALSTON and W. M. SELBY (J. Amer. Chem. Soc., 1939, 61, 1019–1020).—*n*-C₁₁H₂₃·COCl, *n*-C₁₃H₂₇·COCl, *n*-C₁₅H₃₁·COCl, and *n*-C₁₇H₃₅·COCl with Na in hot Et₂O give *μν*-dilauroyl-oxy-Δ⁴-tetracontene, m.p. 42–43°, *ξο*-dimyristoyloxy-Δ⁴-octacosene, m.p. 54–55°, *πρ*-dipalmitoyloxy-Δ⁴-dotriacontene, m.p. 61–62°, and *στ*-distearoyloxy-Δ⁴-hexatriacontene, m.p. 67–68°. Structures are proved by hydrolysis to RCOCl and CH₂R·COR. The reaction mechanism is: 2RCOCl + 2Na → (RCO)₂ → (+2Na) (:CR·ONa)₂ → (+ROCl) (RCO₂·CR)₂. R. S. C.

Chemical examination of sugar-cane wax. N. L. VIDYARTHI and M. NARASINGARAO (J. Indian Chem. Soc., 1939, 16, 135–143).—Sugar-cane wax, extracted by C₆H₆ from the dried press mud of a sulphitation factory, contains 43.7% of acid and 53.6% of unsaponifiable matter. The acids, separated by fractionation of the Et esters, are resin (4.5%), hexoic (0.6%), palmitic (27.7%), stearic (22.4%), oleic (41.5%), and arachidic acid (3.3%). The unsaponifiable matter, separated by treatment with o-C₆H₄(CO)₂O, contains *n*-triacontanol (80%), brassica-, stigma-, and sito-sterol (10%), and *n*-pentatriacontane (5%). The wax contains no dibasic or OH-acids. J. D. R.

Methods of separating oleic acid from saturated acids and from linoleic acid. Preparation of oleic acid. P. J. HARTSUCH (J. Amer. Chem.

Soc., 1939, 61, 1142–1144).—Crude oleic acid from olive- or tea-seed oil is best freed from much saturated acid by dissolution in COMe₂ at –18° to –20°; the material in the filtrate is freed from much linoleic acid by crystallisation from COMe₂ at –60°. The 96% pure product is then fractionally distilled, giving oleic acid containing 1% of linoleic and 1.2% of saturated acids. R. S. C.

Esters of isooleic acids. A. A. TSCHERNOJAROVA (J. Gen. Chem. Russ., 1939, 9, 178–181).—Me, b.p. 196–197°/8 mm., Pr^a, b.p. 199–200°/5 mm., Pr^b, b.p. 192–194°/5–6 mm., Bu^a, b.p. 202–204°/6–7 mm., isoamyl, b.p. 216–217°/5–6 mm., and sec.-octyl petroselate, b.p. 236–239°/5–7 mm., Pr^c, b.p. 198°/10 mm., Bu^b, b.p. 216–218°/8 mm., isoamyl, b.p. 247–250°/15–16 mm., and sec.-octyl isooleate, b.p. 240–241°/6–7 mm., Me, b.p. 214°/7 mm., Pr^a, b.p. 228°/9 mm., Bu^a, b.p. 229°/10 mm., isoamyl, b.p. 241°/9 mm., and sec.-octyl *τ*-chlorostearate, b.p. 254°/9 mm., and Me, b.p. 193–195°/8 mm., Pr^a, b.p. 205–208°/10 mm., Bu^a, b.p. 219°/10 mm., and isoamyl isopetroselate, b.p. 220–222°/8 mm., have been prepared, and the *n*, *d*, and I val. of the esters determined. The position of the double linking does not significantly affect the physical properties of the esters. R. T.

Elaidinisation of linoleic acid. J. P. KASS and G. O. BURR (J. Amer. Chem. Soc., 1939, 61, 1062–1066).—When warmed for a short time with NaNO₂ in 1 : 1 aq. HNO₃ or 1 : 3 H₂SO₄-H₂O, or when heated with a little Se in N₂ at 200–210°, linoleic acid gives *linolelaidic acid* (I), m.p. 28–29° (Pb salt; dibromide, m.p. 78°, insol. in light petroleum), and a mixed liquid β-acid (sol. dibromide). (I) is spectroscopically inactive, is oxidised (after esterification) by KMnO₄ in COMe₂ to hexoic acid and alkyl azelate, or, as acid, by KMnO₄ in aq. NaOH at 0° to γ-, m.p. 122°, and δ-sativic acid, m.p. 146° [names previously reversed (Nicolet *et al.*, A., 1922, i, 320)]. The β-acid gives ε-, m.p. 126°, and ζ-sativic acid, m.p. 158°, and an acid, m.p. 131–135°, which may be η-sativic acid or a mixture. It is concluded that no unchanged linoleic acid remains after treatment and that isomerisation occurs first at the θ- and then at the λ-ethylenic linking. R. S. C.

Structure of petroselic acid. A. A. TSCHERNOJAROVA (J. Gen. Chem. Russ., 1939, 9, 149–152).—Ozonolysis of Me petroselate yields lauric and adipic acid; petroselic acid is therefore Δ⁴-heptadecenoic acid. R. T.

Synthesis of αα'-diketo adipic acid. Its biological importance. F. WILLE (Annalen, 1939, 538, 237–260).—Me₂ cyclobutene-1 : 2-dicarboxylate and H₂O₂ in Et₂O give Me₂ αα'-diketo adipate (60%) (I), double m.p. 98–100° and 164–165° [*bis*-2 : 4-dinitrophenylhydrazone, m.p. 242–243° (decomp.); bisphenylhydrazone, m.p. 143–145° (lit. 130–131°)]. At 120–140° (I) gives the dienol form, Me₂ αα'-dihydroxymuconate (II), m.p. 169–170° (reddish-brown FeCl₃ colour). Hydrolysis of (I) by Ba(OH)₂ gives αα'-diketo adipic (III), decomp. 234° (loss of CO₂ at 110°) [with CH₂N₂ gives (I); *bis*-2 : 4-dinitrophenylhydrazone, m.p. 245° (decomp.)], and αα'-dihydroxymuconic acid (IV), m.p. 226–227° (decomp.)

[in equilibrium with (III) in H_2O]. CH_2N_2 converts (IV) into $\text{Me}_2 \alpha\alpha'$ -dimethoxymuconate, m.p. 116° , which is similarly obtained from (II), whereas (I) gives only oils. With aq. NH_4Ph (III) yields 1-phenylpyrrole-2:5-dicarboxylic acid, m.p. 256 – 259° (Me_2 ester, m.p. 110°), and with H_2O_2 yields CO_2 and $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$. Only the dienol is a reducing agent (dichloroindophenol, methylene-blue; with I in NaHCO_3 gives CHI_3). (III) is determined by its O_2 absorption (10% excess) in aq. NaOH at 38° . Rat kidney, rat liver, and pigeon breast muscle destroy (III) anaerobically, but the rates bear no relation to those for AcCO_2H . Yeast also destroys (III) in O_2 or N_2 , but produces <1 mol. of CO_2 and some acid (traces only of HCO_2H); the reaction is thus not due to co-carboxylase. Fermentation of AcCO_2H thus does not proceed by way of (III).

R. S. C.

Structure of the aldobionic acid from flaxseed mucilage. R. S. TIPSON, C. C. CHRISTMAN, and P. A. LEVENE (J. Biol. Chem., 1939, 128, 609–620).—The aldobionic acid (I) (improved prep.) from flaxseed mucilage on complete methylation ($\text{NaOH-Me}_2\text{SO}_4$, CH_2N_2 , and $\text{Ag}_2\text{O-MeI}$) yields a Me ester of a pentamethyl-methylaldobionide, $\text{C}_{19}\text{H}_{34}\text{O}_{11}$, b.p. 165 – $169^\circ/0.1$ – 0.2 mm., m.p. 93 – 94° (indef.), $[\alpha]_D^{25} +129.8^\circ$ in H_2O , hydrolysed by HCl to $\beta\gamma\delta$ -trimethylgalacturonic acid and 3:4-dimethyl-l-rhamnose (II), which on oxidation with HNO_3 followed by esterification and treatment with NH_2Me yields hydroxydimethoxyglutardimethylamide; (I) is therefore 2-(d-galacturonopyranosido)-l-rhamnose. An improved prep. of (II) from l-rhamnose is described.

J. D. R.

Constitution of arabic acid. I. Isolation of 3-d-galactosido-l-arabinose. F. SMITH (J.C.S., 1939, 744–753).—Arabic acid (I) (prep. from gum arabic by cold, dil. HCl), $[\alpha]_D^{20} -28^\circ$ in H_2O , is hydrolysed by hot $0.01\text{N-H}_2\text{SO}_4$ or hot H_2O (p_{H} 2.2; final $[\alpha]_D +42^\circ$ to $+42.5^\circ$ in H_2O) to ~ 1 mol. each of a degraded arabic acid, l-arabinose, l-rhamnose, and 3-d-galactopyranosido-l-arabinose (II). The sugars are separated by methylation (Me_2SO_4 - NaOH , followed by $\text{Ag}_2\text{O-MeI}$) and subsequent distillation into trimethylmonoglucosides (A) and heptamethyl-3-d-galactopyranosido-1-arabopyranose (III), m.p. 82° , b.p. 180° (bath)/0.7 mm. Hydrolysis (3.5% H_2SO_4) and oxidation (Br; 30°) of (A) gives lactones, separated by conversion into 2:3:4-trimethyl-l-arabon-phenylhydrazide and -amide and 2:3:4-l-rhamnonphenylhydrazide, thus proving the nature of the monosaccharides. Since (III) has $[\alpha]_D^{18} +162^\circ$ in H_2O , the biose linking may be of the α -type. The structure of (I) is proved as follows. 7% H_2SO_4 hydrolyses (III) to inseparable glucosides (B), which with $\text{MeI-Ag}_2\text{O}$ give 2:3:4:6-tetramethyl- β -methylgalactopyranoside (IV) and 2:3:4-trimethylmethyl-l-arabopyranoside (V), identified by conversion (Br, followed by NH_3 - MeOH) into the amides. Since (V) is obtained also from (B), the reducing group of the galactose provides the biose link. The nature of (B) is also proved by prep. of 2:3:4:6-tetramethylgalactose-anilide (VI) by $\text{NH}_2\text{Ph-MeOH}$ and of 2:4-dimethyl-l-arabonolactone, $[\alpha]_D^{18} +85^\circ \rightarrow +27^\circ$ in H_2O in 14.5 hr. (therefore a δ -lactone) (with NH_3 - MeOH gives 2:4-

dimethyl-l-arabonamide, m.p. 158° , which gives a negative Weerman reaction and thus has OMe at $\text{C}_{(2)}$). The $\text{C}_{(1)}$ of the galactose is thus joined to the $\text{C}_{(3)}$ of the arabinose. The dimethylarabinose remaining after removal of the (VI) is converted by HNO_3 (d 1.2) at 50° into β -hydroxy- $\alpha\alpha'$ -dimethoxy-l-araboglutaric acid [Me_2 ester, b.p. 115° (bath)/0.02 mm., $[\alpha]_D^{18} +41.3^\circ$ in MeOH ; diamide, m.p. 285° (decomp.), $[\alpha]_D^{18} +62.1^\circ$ in H_2O]. Autolysis of (I) and subsequent treatment with $\text{MeI-Ag}_2\text{O}$ yields 2:3:5-trimethyl-l-arabo- and -methyl-l-rhamno-furanoside and heptamethyl-3-d-galactopyranosido-l-arabofuranose (VII), b.p. 170 – 180° (bath)/0.01 mm., $[\alpha]_D +102^\circ$ in H_2O . Hydrolysis of (VII) by H_2SO_4 gives (IV) and 2:5-dimethyl-l-arabinose (VIII), $[\alpha]_D^{18} +46.6^\circ$ in H_2O ; the latter product is oxidised to 2:5-dimethyl- γ -l-arabonolactone, m.p. 60° , $[\alpha]_D^{18} -59.7^\circ \rightarrow <-44.8^\circ$ in H_2O (free acid, $[\alpha]_D^{18} +25.8^\circ \rightarrow -16.0^\circ$ in H_2O in 120 hr.), which gives 2:5-dimethyl-l-arabonamide, m.p. 131° , $[\alpha]_D^{18} +38^\circ$ in H_2O (negative Weerman test), or (by $\text{MeI-Ag}_2\text{O}$) 2:3:5-trimethyl- γ -l-arabonolactone and thence the derived amide. 2:3-Dimethyl-l-arabinose differs from (VIII), which has thus the structure cited. Since (I) is so readily hydrolysed, it probably contains (II) in the arabofuranose form. 3- β -d-Galactosido-d-arabinose (prep. from lactose; isolated as benzylphenylhydrazone and regenerated therefrom by PhCHO) with Me_2SO_4 - $\text{NaOH-H}_2\text{O-COMe}_2$ gives a Me_6 , m.p. 136° , $[\alpha]_D^{18} -12.1^\circ$ in MeOH , and Me_7 ether, hydrolysed by 4% H_2SO_4 to an inseparable mixture of 2:3:4:6-tetramethylgalactose and 2:4-dimethyl-d-arabinose. The latter product gives 2:4-dimethyl-d-arabinoseanilide, m.p. 142 – 143° , (by Br) 2:4-dimethyl-d-arabonolactone, $[\alpha]_D^{22} -85^\circ \rightarrow -33.0^\circ$ in H_2O in 18 hr. (derived amide, m.p. 158° , $[\alpha]_D^{17} -58.8^\circ$ in H_2O), and (by HNO_3) β -hydroxy- $\alpha\alpha'$ -dimethoxy-d-araboglutaric acid [Me_2 ester, b.p. 135° (bath)/0.12 mm., $[\alpha]_D^{18} -32^\circ$ in MeOH ; diamide, m.p. 286° (decomp.), $[\alpha]_D^{17} -62.8^\circ$ in H_2O], enantiomorphic with, and thus confirming the structures of, the products derived from (I).

R. S. C.

Mode of union of the galacturonic residues in pectic acid. P. A. LEVENE, G. M. MEYER, and M. KUNA (Science, 1939, 89, 370).—Exhaustive methylation of pectic acid gives $\text{C}_{56}\text{H}_{90}\text{O}_{37}$ (OMe 45–40%) (I) corresponding with a structure composed of ~ 6 units. Hydrolysis of (I) gives $\text{C}_{50}\text{H}_{78}\text{O}_{37}$ (OMe 34–30%). The methylated polygalactoside, $\text{C}_{56}\text{H}_{102}\text{O}_{31}$ (OMe 47–33%), has been prepared by heating the exhaustively methylated material with Cu chromite catalyst in H_2 at $175^\circ/3500$ lb. per sq. in. for 6 hr. The rate of hydrolysis of the fully methylated pectic acid indicates a furanose structure for the galacturonic residues, the union of which is thus through $\text{C}_{(5)}$.

L. S. T.

Reaction of iron with thioglycollic acid.—See A., 1939, 1, 387.

Mechanism of the formation of the dichloride of sulphoacetic acid. Multimolecular chloroanhydrides of sulphoacetic acid. R. VIEILLE-ROSSE (Compt. rend., 1939, 208, 1505–1507).— $\text{SO}_3\text{H-CH}_2\cdot\text{CO}_2\text{H}$ when boiled with excess of SOCl_2 affords little $\text{SO}_2\text{Cl-CH}_2\cdot\text{COCl}$ but when the excess of SOCl_2 is removed by heating in vac., a prolonged

liberation of gas occurs with the formation of a multimol. product (I) (Cl determination and acid liberated in contact with H_2O) which is unstable and usually consists of a mixture of compounds derived from 2 or 3 units of $SO_3H \cdot CH_2 \cdot COCl$.

$SO_2Cl \cdot CH_2 \cdot CO_2H$ is only slowly decomposed on prolonged heating.

J. L. D.

Action of periodic acid on acetone and diethyl ketone. P. FLEURY and R. BOISSON (Compt. rend., 1939, 208, 1509—1512).— $0.1N \cdot COMe_2$ when treated with $0.05\text{--}0.2N \cdot HIO_4$ at 37° utilises one O per mol. of $COMe_2$ in 5 days. At 100° a max. of 3 O per mol. is used to give $AcOH$ and CH_2O . $MeOH$ may be an initial reaction product (cf. A., 1937, II, 273) which is oxidised by HIO_4 in presence of $COMe_2$. Similarly treated, $COEt_2$ gives $EtCO_2H$ and $EtOH$. The ketones probably exist as the $C(OH)_2$ derivatives before scission of the C chain.

J. L. D.

Mechanism of contact hydrogenation of carbonyl groups in presence of metallic catalysts.—See A., 1939, I, 377.

Keto-ethers derived from α -chloroethyl sec.-butyl ether. R. J. SPEER with H. R. HENZE (J. Amer. Chem. Soc., 1939, 61, 1226—1227).—*Paracetaldehyde, sec.-BuOH*, and HCl give 83% of *CHMeCl sec.-Bu ether*, b.p. 109° (decomp.)/741 mm., $38\text{--}39^\circ$ (slight decomp.)/20 mm., converted by $AgCN$ in C_6H_6 into *CHMeCN sec.-Bu ether*, b.p. $162^\circ/744$ mm. This and the appropriate Grignard reagent give *Me*, b.p. $162\text{--}163^\circ/750$ mm. (*semicarbazone*, m.p. $117\text{--}118^\circ$), and *Et*, b.p. $174^\circ/747$ mm., α -*sec.-butoxyethyl ketone* (*semicarbazone*, m.p. $126\text{--}127^\circ$), α -*sec.-butoxyethyl Pr^u*, b.p. $189^\circ/750$ mm. (*semicarbazone*, m.p. 116°), *Pr^u*, b.p. $186^\circ/751$ mm. (no *semicarbazone*), *Bu^u*, b.p. $212^\circ/750$ mm. (*semicarbazone*, m.p. $106\text{--}107^\circ$), *Bu^u*, b.p. $202^\circ/747$ mm. (*semicarbazone*, m.p. 100°), *sec.-Bu*, b.p. $206^\circ/751$ mm. (no *semicarbazone*), *n-amyl*, b.p. $226^\circ/745$ mm. (*semicarbazone*, m.p. 78°), and *isomyl*, b.p. $221^\circ/747$ mm. (*semicarbazone*, m.p. 104°), *ketone*. The ketones do not condense with isatin. M.p. are corr.

R. S. C.

Synthesis of aldehyde-sugars. C. D. HURD and E. M. FILACHIONE (J. Amer. Chem. Soc., 1939, 61, 1156—1159).—Compounds, $RCO_2 \cdot CHR' \cdot CH \cdot CH_2$, are converted by O_3 into $RCO_2 \cdot CHR' \cdot CHO$, if the ozonide is decomposed by 20% aq. $AcCO_2H$, the $AcCO_2H$ removing the H_2O_2 and largely preventing formation of the acid. Thus, $CH_2 \cdot CH \cdot CH_2 \cdot OBz$, b.p. $122\text{--}123^\circ/24$ mm., gives 56% of benzoyloxyacetaldehyde (2:4-dinitro-, m.p. $186\text{--}187^\circ$, and *p-nitro-phenylhydrazone*, m.p. $155\text{--}156^\circ$), but only 25% of aldehyde and 47% of $OBz \cdot CH_2 \cdot CO_2H$ if H_2O alone is used. $CH_2 \cdot CH \cdot CH_2 \cdot OAc$ gives $OH \cdot CH_2 \cdot CHO$, $OH \cdot CH_2 \cdot CO_2H$, and $AcOH$, hydrolysis also occurring. *Erythrol dibenzoate*, b.p. $199\text{--}200^\circ/6$ mm., gives *dibenzoyl-dl-glycerose* (70%), m.p. $55\text{--}56^\circ$ (2:4-dinitrophenylhydrazone, m.p. $151\text{--}152^\circ$), and 20% of *dibenzoyl-dl-glyceric acid*, m.p. $88\text{--}89^\circ$. *Mannitol triformate* (prep. by 80% HCO_2H at 140°), m.p. $108\text{--}111^\circ$, $[\alpha]_D^{25} +10.4^\circ$ in $COMe_2$, and O_3 give, among other products, impure (?) 2-vinyl-, b.p. $104\text{--}107^\circ$, and (?) 2- α -hydroxy-*formoxyethyl-2:5-dihydrofuran*, b.p. $135\text{--}142^\circ/17$ mm., $[\alpha]_D^{25} -32.9^\circ$ in $CHCl_3$. Triacetylglucal is hydro-

lysed during the reaction, giving $AcOH$, di- and tri-acetylalabinose.

R. S. C.

Preparation of *d*-erythrulose. K. IWADARE (Bull. Chem. Soc. Japan, 1939, 14, 131—134).—Prep. of isopropylidene-*d*-mannitol and thence by $Pb(OAc)_4$ of isopropylidene-*d*-glyceraldehyde (I) is described. With $KOH \cdot KMnO_4$ (I) gives *K isopropylidene-d-glycerate*, $[\alpha]_D^{15} +23.7^\circ$ in H_2O , the acid chloride, b.p. $61^\circ/15$ mm., $[\alpha]_D^{15} +14.9^\circ$ in Et_2O , from which is converted into the *amide*, m.p. $72\text{--}73^\circ$, $[\alpha]_D^{15} +39.1^\circ$ in H_2O , or by $CH_3N_2 \cdot Et_2O$, followed by hot 1% H_2SO_4 , into *d-erythrulose*, b.p. $68^\circ/0.01$ mm., $[\alpha]_D^{15} -11.6^\circ \pm 3^\circ$ in (?) H_2O . The structure of the sugar is shown by its yielding *d*-threosazone, m.p. 168° .

R. S. C.

2:3-Dimethyl-*l*-arabinose and its derivatives. F. SMITH (J.C.S., 1939, 753—755).—Methyl-*l*-arabofuranoside gives the 5-*CPh₃ ether*, $[\alpha]_D^{20} -17^\circ$ in $CHCl_3$, converted by $MeI \cdot Ag_2O$ into 5-triphenylmethyl-2:3-dimethylmethyl-*l*-arabofuranoside, $[\alpha]_D^{20} -12.3^\circ$ in $CHCl_3$, which with $HCl \cdot CHCl_3$, followed by $HCl \cdot MeOH$, gives 2:3-dimethylmethyl-*l*-arabinoside, b.p. 86° (bath)/0.04 mm. 3% H_2SO_4 then gives 2:3-dimethyl-*l*-arabinose, $[\alpha]_D^{15} +86.4^\circ \rightarrow +107^\circ$ in 2.5 hr. in H_2O (*anilide*, m.p. 139°), which yields 3-methyl-*l*-arabinose-phenylosazone, m.p. 163° , and (by Br) 2:3-dimethyl- γ -*l*-arabonolactone, b.p. 120° (bath)/0.03 mm., $[\alpha]_D^{15} -36^\circ \rightarrow -27^\circ$ in 11 days in H_2O (gives the *amide*, m.p. 162° , $[\alpha]_D^{21} +17.4^\circ$ in H_2O ; negative Weerman test; free acid, $[\alpha]_D^{15} +8.2^\circ \rightarrow -25.4^\circ$ in aq. H_2SO_4 in 74 hr.), converted by HNO_3 (d 1.42) into α -hydroxy- β - α' -dimethoxy-*l*-araboglutaric acid [*Me₂ ester*, b.p. 140° (bath)/0.02 mm., $[\alpha]_D^{20} +6^\circ$ in H_2O ; *diamide*, m.p. 195° , $[\alpha]_D^{21} +26.8^\circ$ in H_2O].

R. S. C.

Synthesis of 2:4:6-trimethylglucose. J. W. H. OLDHAM and M. A. OLDHAM (J. Amer. Chem. Soc., 1939, 61, 1112—1113).—Treating diisopropylidene-glucose 3-*p*-toluenesulphonate successively with $HCl \cdot H_2O \cdot MeCN$, $Ac_2O \cdot C_6H_5N$, $HCl \cdot AcOH$, and $MeOH \cdot Ag_2CO_3$ gives β -methyl-2:4:6-trimethylglucoside 3-*p*-toluenesulphonate, but the α -form cannot be obtained. 4:6-Benzylidene- β -methylglucoside 3-*p*-toluenesulphonate (prepared by $PhCHO$ and $ZnCl_2$), m.p. $174\text{--}176^\circ$ (decomp.), $[\alpha]_D -93.3^\circ$ in $CHCl_3$, could not be methylated. Diisopropylidene-glucose 3-*p*-toluenesulphonate and 2% $HCl \cdot MeOH$ give a product, methylated to α -methyl-2:4:6-trimethylglucoside 3-*p*-toluenesulphonate, m.p. $123\text{--}124^\circ$, $[\alpha]_D +53.6^\circ$ in $CHCl_3$. β -Methyl-2-methylglucoside, $PhCHO$, and $ZnCl_2$ give 4:6-benzylidene-2-methyl- β -methylglucoside, m.p. $170\text{--}171^\circ$, $[\alpha]_D -69.2^\circ$ in $CHCl_3$, methylated to 4:6-benzylidene-2:3-dimethyl- β -methylglucoside and converted by $p\text{-C}_6H_4Me \cdot SO_2Cl$ into 4:6-benzylidene-2-methyl- β -methylglucoside *p*-toluenesulphonate, m.p. $135\text{--}136^\circ$. Hydrolysis then removes $CHPh$ and methylation gives 2:4:6-trimethyl- β -methylglucoside 3-*p*-toluenesulphonate, m.p. $103\text{--}104^\circ$, $[\alpha]_D +1.9^\circ$ in $CHCl_3$, also obtained from 2:4:6-trimethyl- β -methylglucoside. The structure of 2:4:6-trimethylglucose is thus proved.

R. S. C.

Carbohydrates. XXI. Ethylthioglucofuranosides and 5:6-isopropylideneglucose. P. BRIGL, K. GRONEMEIER, and A. SCHULZ (Ber., 1939, 72, [B], 1052—1059).—Glucose Et_2 mercaptal (I) is converted

by glucose in 22% HCl at room temp. followed by acetylation into α -ethylthioglucofuranoside tetra-acetate, m.p. 97.5°, $[\alpha]_D^{20} +189.6^\circ$ in $C_2H_5Cl_4$, +207° in EtOH, hydrolysed by $Ba(OH)_2$ to α -ethylthioglucofuranoside (II), m.p. 117°, $[\alpha] +269^\circ$ in H_2O , which is non-reducing and evolves EtSH when heated with conc. HCl. (I) is converted by $COMe_2$ containing $CuSO_4$ with 21% of H_2O into 5:6-isopropylideneglucose Et_2 mercaptal, m.p. 74–75°, $[\alpha] -6.6^\circ$ in EtOH (triacetate, m.p. 84.5°), converted by $HgCl_2$ in not too strongly acid solution into 5:6-isopropylidene-ethylthioglucofuranoside, m.p. 103°, $[\alpha] +114.5^\circ$ in EtOH; this compound is also obtained from the α -form of Schneider and Sepp (A., 1916, I, 792), which must therefore be α -ethylthioglucofuranoside, leaving the pyranoside structure available for (II). Gradual addition of (II) in aq. $COMe_2$ to a mixture of $BaCO_3$ and $HgCl_2$ in H_2O at 50° gives 5:6-isopropylidene-glucose, m.p. 120°, $[\alpha]_D^{20} +10.5^\circ$ in H_2O , which reduces Fehling's solution strongly and gives a colour with fuchsin- H_2SO_4 . It is converted by $COMe_2$ and anhyd. $CuSO_4$ into diisopropylideneglucose, m.p. 110°.

H. W.

Behaviour of sulphoxides towards sulphite. F. MICHEEL and H. SCHMITZ (Ber., 1939, 72, [B], 992–994).—Thio-ethers are stable towards SO_3 , and α -ethyl-d-thiogluconoside (I), m.p. 156°, $[\alpha]_D^{18} +120.0^\circ$ in H_2O , is not attacked thereby; the production of minute amounts of mercaptan after prolonged action is ascribed to simple hydrolysis in the somewhat acidic medium ($p_H \sim 4.5$). Oxidation of (I) with 30% H_2O_2 in H_2O at 0° affords α -ethyl-d-glucosidosulphoxide (II), m.p. 120°, $[\alpha]_D^{18} +45.7^\circ$ in H_2O , the persistence of the sugar chain in which is established by the production of a tetra-acetate, m.p. 139°, $[\alpha]_D^{18} +21.4^\circ$ in EtOH. dl-Methionine is transformed by AcO_2H into the sulphoxide which, like (II), is reduced by $Na_2S_2O_5$ to the corresponding sulphide, fission of the C-S linking not being observed. l-Cystine disulphoxide reacts with $Na_2S_2O_5$ without formation of the SH group.

H. W.

β -d-2-Deoxygalactose. H. S. ISBELL and W. W. PIGMAN (J. Res. Nat. Bur. Stand., 1939, 22, 397–402).—Galactal in 5% aq. H_2SO_4 after keeping overnight at 0°, followed by agitation (50 hr.; 60°) with gradual addition of excess of $BaCO_3$, and final concn. affords β -d-2-deoxygalactose, m.p. 120–121°, $[\alpha]_D^{20} +41^\circ \rightarrow +37^\circ$ in 5 min. $\rightarrow +60.5^\circ$ (final) in H_2O buffered with 0.001N-K H phthalate. The observed mutarotation indicates that equilibrium is established between an α -pyranose modification and a labile substance.

F. N. W.

Action of baker's yeast on d-talose.—See A., 1939, III, 724.

aldehydo-Derivatives of D- α -galactose (D-gala-L-galactose). R. W. HANN, W. D. MACLAY, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1270–1271).—D-Gala-L-galactose Et mercaptal (prep. in conc. aq. HCl), m.p. 214°, $[\alpha]_D^{20} -3.2^\circ$ in dry C_5H_5N , gives a hepta-acetate, m.p. 106°, $[\alpha]_D^{20} +29.9^\circ$ in $CHCl_3$, converted by $HgCl_2$ - $CdCO_3$ in $COMe_2$ into aldehydo-D-gala-L-galactose hepta-acetate (I), m.p. 164–165°, $[\alpha]_D^{20} +71.3^\circ$ in $CHCl_3$ (semicarbazone, m.p. 203–204°, $[\alpha]_D^{20} -27.0^\circ$ in $CHCl_3$). This yields the oxime

hepta-acetate, m.p. 179–179.5°, $[\alpha]_D^{20} +20.2^\circ$ in $CHCl_3$, and thence by C_5H_5N - Ac_2O the oxime octa-acetate, m.p. 187–188°, $[\alpha]_D^{20} +14.9^\circ$ in $CHCl_3$. Boiling with Ac_2O - $NaOAc$ or heating alone at 190° then gives D-gala-L-gala-octononitrile hepta-acetate, m.p. 185°, $[\alpha]_D^{20} +8.5^\circ$ in $CHCl_3$. With 2% of H_2SO_4 in 1:1 Ac_2O - $AcOH$ (I) gives the nona-acetate, m.p. 149–150°, $[\alpha]_D^{20} +26.1^\circ$ in $CHCl_3$. D-Galactose Et_2 mercaptal, m.p. 142–143°, has $[\alpha]_D^{20} -3.5^\circ$ in C_5H_5N , +6.0° in EtOH, and -4.8° in H_2O . $[\alpha]$ of these compounds show no parallelism with those of the L-galactose series. These and previous results show that the relations existing among cyclic sugars do not hold for open-chain derivatives. M.p. are corr. R. S. C.

Relations between rotatory power and structure in the sugar group. XXXI. Configuration of D- α -manno-octose (D-manno-L-manno-octose). R. M. HANN, W. D. MACLAY, A. E. KNAUF, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1268–1269; cf. A., 1930, 1023).—Identification of Fischer's D- α -manno-octose as D-manno-L-manno-octose is confirmed. The derived lactone with liquid NH_3 gives D-manno-L-manno-octonamide, m.p. 218–219° (rapid heating), $[\alpha]_D^{20} +9.8^\circ$ in H_2O [octa-, m.p. 172–173° (corr.), $[\alpha]_D^{20} +15^\circ$ in $CHCl_3$, and hepta-acetate, m.p. 99–100° (corr.), $[\alpha]_D^{20} -15.9^\circ$ in $CHCl_3$], and with Na-Hg, followed by H_2 -Raney Ni at 98°/133 atm., gives D-manno-L-manno-octitol, m.p. 262–263° (corr.) [octa-acetate, m.p. 166–167° (corr.), $[\alpha]_D^{20} 0$ in $CHCl_3$].

R. S. C.

Caramelisation of sucrose with sulphuric acid. J. MILBAUER (Chem. Listy, 1939, 33, 132–133).—The process of caramelisation of aq. sucrose in 6M- H_2SO_4 is followed with the aid of a photo-electric cell. Addition of $HgSO_4$ does not accelerate the process.

R. T.

Sucrose octa-acetate. K. ŠANDERA (Chem. Listy, 1939, 33, 139–141).—Sucrose octa-acetate is prepared on a laboratory scale from Ac_2O and sucrose in C_5H_5N at 100–115°.

R. T.

Carpotroside, a new glycoside or heteroside from sapucainha (Carpotriche brasiliensis, Endl). R. D. DE G. PAULA (Rev. Soc. Brasil. Quím., 1938, 7, 129–140).—The cake from sapucainha seeds after extraction of the oil contains 0.4% of H_2O -sol. carpotroside (formerly called carpotrochin), $(C_6H_{10}NO_3)_n$, blackens about 260°, $[\alpha]_D^{20} -7.106^\circ$. Acid hydrolysis gives $PhCHO$, an unidentified sugar, an aldehyde, and an indole derivative. No recognisable products were obtained by enzymic hydrolysis.

F. R. G.

Saponin of Sarcostemma australe, R. Br. J. W. CORNFORTH and J. C. EARL (J.C.S., 1939, 737–742).—This saponin (I) (Earl *et al.*, A., 1937, III, 245) is sol. in org. solvents and is purified by partition. It is mainly a mixture of sarcostin benzoate cinnamate d-glucosides. With 0.75% HCl-MeOH at 100° it gives an aglucone (II) and α -methylglucoside, and with boiling HCl-aq. EtOH gives (II) and d-glucose (isolated as phenylosazone; 1 mol. obtained by dil. H_2SO_4). With hot KOH-EtOH (II) gives 1 mol. each of $BzOH$, $CHPh:CH:CO_2H$, and sarcostin (III), $C_{21}H_{34}O_8$, + H_2O (lost at 100°/vac. over P_2O_5), m.p. 266–267° after sintering or 170° (rapid heating);

resolidifies) [triacetate (prep. by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$), a resin, regenerates (III) when hydrolysed]. With $\text{KOH}-\text{EtOH}$, followed by $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$, (I) gives *sarcosin glucoside hexa-acetate*, a resin. Adsorption (Al_2O_3) shows (II) to consist almost entirely of *sarcosin benzoate cinnamate*. Hydrolysis of (I) indicates the presence of monoacylated derivatives, but these are probably not originally present and the results follow from the instability in acid. (I), (II), and (III) give the Liebermann-Burchard test; (I) and (II) give the Legal test weakly. R. S. C.

The α -*D*-mannoside of sodium *L*-glycerate in the genus *Polysiphonia* of the Floridaceæ. H. COLIN and J. AUGIER (Compt. rend., 1939, 208, 1450—1453).—EtOH extracts *Na* α -*D*-mannoside-*L*-glycerate, decomp. at 270° after darkening at $\sim 245^\circ$, $[\alpha]_D^{20} +108^\circ$, which with hot 2% H_2SO_4 gives mannose (60% yield); with sufficient cold H_2SO_4 it affords hydrated α -*D*-mannoside-*L*-glyceric acid, m.p. $88-89^\circ$, $[\alpha]_D^{25}$ of anhyd. material $+105^\circ$, easily hydrolysed by excess of acid to mannose and *L*-glyceric acid. *P. fruticulosa* also contains the glucoside.

J. L. D.

Water-soluble glucosan from barley roots. W. Z. HASSID (J. Amer. Chem. Soc., 1939, 61, 1223—1225).—Extraction of barley roots with 95% EtOH gives 0.4% of a H_2O -sol. glucosan, $[\alpha]_D^{20} +201^\circ$ in H_2O (Ac_2 derivative, $[\alpha]_D^{20} +112^\circ$ in CHCl_3), hydrolysed to glucose only and giving a Me_3 ether, $[\alpha]_D^{20} +204^\circ$ in CHCl_3 , which with (a) $\text{HCl}-\text{AcOH}$ at 100° gives 2:3:6-trimethylglucose and (b) $\text{HCl}-\text{MeOH}$ gives 2:3:4-trimethyl- β -methylglucoside. The glucose units are thus probably united by 1—6 linkings.

R. S. C.

Pine bark. I. E. LEHMANN and F. EISENHUTH (Ber., 1939, 72, [B], 1003—1011).—The bark is extracted with org. solvents, mainly EtOH, to remove fats and waxes. Separation of skeleton substance (I) from phlobaphen pigment (II) is incomplete with Na_2CO_3 but nearly quant. with alkali hydroxide. The alkaline solution gives the pigment in degraded form when acidified (54—55% of the extracted bark). (I), thus obtained, is a coffee-brown material from which the remnants of (II) can be removed by the very protracted action of $\text{AcOH}-\text{H}_2\text{O}_2$, which also causes some degradation of (I). Treatment with SO_3 causes the production of Na salts of sulphonic acids sol. in H_2O ; a small proportion of (II) remains which can be removed by H_2SO_3 , leaving (I) as a pale grey mass ($\sim 20-22\%$ of the crude bark) in which cellulose fibres and woody fragments are noticeable. After treatment of (I) with Et_2O , (I) results containing 8% of ash which is almost entirely loose sand and can be reduced to 2% by use of CCl_4 . Analyses shows this to be a polysaccharide $[(\text{C}_6\text{H}_{12}\text{O}_6)_2(\text{C}_6\text{H}_{10}\text{O}_5)_3]_x$ or $[(\text{C}_6\text{H}_{12}\text{O}_6)_3 - 3\text{H}_2\text{O}]_x$. To remove the remainder of the sand from (I) the product is repeatedly evaporated with 40% HF, whereby the incidental hydrolysis occurs so slowly that it is obvious that (I) is of unusual structure and a means is also afforded of obtaining (I) very pure. Its analytical composition remains unaffected. The product of the hydrolysis by HF reduces Fehling's solution, possibly owing to glucose formed from admixed cellulose. When

treated with $\text{C}_5\text{H}_5\text{N}$ and Ac_2O it gives a *pentasaccharide acetate*, m.p. 143° , which has no reducing power so that the saccharide is presumably of the trehalose type. Treatment of (I) under mild conditions with HCl , HBr , H_2SO_3 , or H_2SO_4 is without effect whereas under more drastic circumstances carbonisation takes place. With 75% H_2SO_4 galactose (III) is produced. Pentosans and cellulose are shown to be merely attendants of the precursor of (III) since (I) obtained after treatment with CCl_4 (see above) is sol. in Schweitzer's solution which on acidification gives (I) with the composition $\text{C}_6\text{H}_{12}\text{O}_6$ and the properties of a polysaccharide of very high mol. wt.; this with 75% H_2SO_4 again gives (III), which is therefore a component of (I). Tentative formulæ are proposed for (I) and the pentasaccharide. H. W.

Mucopolysaccharide from synovial fluid.—See A., 1939, III, 597.

Starch. M. SAMEO (Chem.-Ztg., 1939, 63, 353—357).—A review.

Isolation of a crystalline substance from starches oxidised by periodate. D. H. GRANGAARD, J. H. MICHELL, and C. B. PURVES (J. Amer. Chem. Soc., 1939, 61, 1290—1291).—Treatment of maize, wheat, potato, or arrowroot starch with $\text{Na}_2\text{H}_2\text{IO}_6-\text{AcOH}$ and then with 10% $\text{HCl}-\text{MeOH}$ (dry) gives 0.7—0.9% of a substance, $\text{C}_{13}\text{H}_{16}\text{O}_3(\text{OMe})_4$, m.p. $150-150.5^\circ$ (corr.), $[\alpha]_D^{25} -7.1^\circ$ in dioxan.

R. S. C.

Fractionation of cellulose. H. TYDÉN (Svensk Kem. Tidskr., 1939, 51, 100—101).—Fractionation of cellulose (from $\text{Cu}^{++}-\text{NH}_4^+$ solution) from $\text{ZnO}-\text{NaOH}$ ($>2\text{N}$. to prevent pptn. of ZnO during fractionation) with 10% aq. Na_2SO_4 takes 12 hr. and yields the longer chain mols. first.

M. H. M. A.

Molecular size of methylated cellulose. M. L. WOLFRAM, J. C. SOWDEN, and E. N. LASSETTRE (J. Amer. Chem. Soc., 1939, 61, 1072—1076).—The Me_3 ether of commercial COMe_2 -sol. cellulose acetate is hydrolysed by HCl ($d\ 1.2$) in presence of EtSH at 0° . Determination of S in the product shows the degree of polymerisation to be 150 after 3.5 and 50 after 17 hr. and, by mathematical and graphical analysis, to be 400 ± 70 for the original Me_3 ether. η for the acetate shows it to contain 350 ± 35 glucose units. Changes in $[\alpha]$ for the ether in HCl at 24° are recorded; the final val. is that of trimethyl-*D*-glucose. R. S. C.

Action of aqueous ammonia on halogeno-derivatives. Preparation of aliphatic diamines. G. DARZENS (Compt. rend., 1939, 208, 1503—1504).— $\text{CHMeCl}-\text{CH}_2\text{Cl}$ (1 mol.) with a large excess of 34% aq. NH_3 at $75-80^\circ/8$ days gives $\alpha\beta$ -diaminopropane (92%), b.p. $120^\circ/760$ mm., and a little CMe_2CH . Reaction in abs. EtOH occurs only at 120° and a complex mixture of bases is formed. With anhyd. NH_3 a mixture results. Bu^nBr or Bu^nCl with aq. NH_3 at 65° affords CMe_2CH_2 (100%). $\text{CH}_2\text{Ph}-\text{CH}_2\text{Br}$ gives $(\text{CHPhCH}_2)_n$. CH_2PhCl gives $\text{CH}_2\text{Ph}-\text{NH}_2$, $\text{NH}(\text{CH}_2\text{Ph})_2$, and $\text{N}(\text{CH}_2\text{Ph})_3$; amyl bromide gives similar products. J. L. D.

Aliphatic polyamines. VIII. J. VAN ALPHEN (Rec. trav. chim., 1939, 58, 544—549; cf. A., 1938, II, 175).— $\alpha\kappa$ -Dibromodecane and $(\text{CH}_2-\text{NH}_2)_2\cdot\text{H}_2\text{O}$ in

EtOH, then KOH, afford $\alpha\kappa$ -di(aminoethylamino)-decane (I), m.p. 37° (tetrapicrate, m.p. 194°), with some hexamine derivative,

$(\text{NH}_2 \cdot [\text{CH}_2]_2 \cdot \text{NH} \cdot [\text{CH}_2]_{10} \cdot \text{NH} \cdot \text{CH}_2)_2$, m.p. 36° (hexaphenylthiocarbamyl derivative, m.p. ~106°, indicates straight chain), and higher condensation products (m.p. 46°). (I) and PhNCO in Et₂O give $\alpha\kappa$ -di-(phenylcarbamidoethyl-phenylcarbamyl)aminodecane, m.p. 207°; PhNCS affords the thiocarbamyl analogue, m.p. 185°. (I) and CS₂ in EtOH give an adduct, decomp. 80–105°, of (I) + 2CS₂, decomp. at 140° to $\alpha\kappa$ -di-(2'-thio-1' : 3' : 4' : 5'-tetrahydroiminazolo)decane, $(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CS})_2 [\text{CH}_2]_{10}$, m.p. 166°. (I) and PhCHO

give a condensation product, which with Na-EtOH gives (method: A., 1936, 1493) $\alpha\kappa$ -di(benzylaminoethylamino)decane [tetrahydrochloride (II), m.p. 265° (decomp.)], converted by PhCHO in Et₂O into $\alpha\kappa$ -di-(2'-phenyl-3'-benzyl-1' : 2' : 4' : 5'-tetrahydroiminazolo)decane, m.p. 139°, decomposed by dil. HCl to PhCHO and (II). A. T. P.

Synthesis of glucosamine. W. O. CUTLER and S. PEAT (J.C.S., 1939, 782–783).—The structure of glucosamine is confirmed by prep. of 2-aminotrimethyl- β -methylglucopyranoside (isolated as Ac derivative, m.p. 195°, $[\alpha]_D^{25}$ –29.4° in H₂O) in poor yield from 3 : 4 : 6-trimethyl- β -methylglucoside 2-*p*-toluenesulphonate and dry NH₃-MeOH at 175° (cf. A., 1939, II, 144). R. S. C.

New acetylated derivatives of amino-sugars. G. J. ROBERTSON and W. H. MYERS (Nature, 1939, 143, 640–641).—Acetylation of the material obtained by the action of NH₃ on 2 : 3-anhydro-4 : 6-benzylidene- α -methylalloside gives a 60% yield of 2-acetamido-3-acetyl-4 : 6-benzylidene- α -methylaltroside, m.p. 181–182°, $[\alpha]_D^{25}$ +51.3° in CHCl₃, and 1% of 3-acetamido-2-acetyl-4 : 6-benzylidene- α -methylglucoside, m.p. 266°, $[\alpha]_D^{25}$ +45.6° in CHCl₃ (cf. A., 1938, II, 348). Similar treatment of 2 : 3-anhydro-4 : 6-benzylidene- α -methylmannoside gives 60% of 3-acetamido-2-acetyl-4 : 6-benzylidene- α -methylaltroside (I), m.p. 201°, $[\alpha]_D^{25}$ +14.6° in CHCl₃, and ~1% of 2-acetamido-3-acetyl-4 : 6-benzylidene- α -methylglucoside, m.p. 235°, $[\alpha]_D^{25}$ +45.5° in CHCl₃. Galactose has been converted into a 2 : 3-anhydro-4 : 6-benzylidene- α -methylhexoside which has either the gulose or the talose configuration. Acetylation following the action of NH₃ on this substance gives two isomeric 4 : 6-benzylideneamino- α -methylhexoside diacetates, m.p. 188°, $[\alpha]_D^{25}$ +43.4° in CHCl₃ and m.p. 260°, $[\alpha]_D^{25}$ +70.3° in CHCl₃. The same treatment of the α -methylhexoside chlorohydrin, m.p. 160°, reported previously (*ibid.*, 218) yields (60%) 3-acetamido- α -methylglucoside triacetate (II), m.p. 179°, $[\alpha]_D^{25}$ +105.9° in CHCl₃ (cf. *ibid.*, 348), and a trace of an unidentified isomeride, m.p. 130°, $[\alpha]_D^{25}$ +95.7° in CHCl₃, whilst the other chlorohydrin, m.p. 138° (*ibid.*, 218) yields 50% of (II) and 20% of an isomeride, $[\alpha]_D^{25}$ +50.4° in CHCl₃, not yet identified. 2 : 3-Anhydro-4 : 6-benzylidene- α -methylmannoside gives a syrupy mixture of α -methylhexoside chlorohydrins which when treated with NH₃ followed by acetylation yields 15% of (II) and 65% of an isomeride (III), m.p. 177°, $[\alpha]_D^{25}$ +34.7° in CHCl₃. Removal of :CHPh

from (I) and acetylation of the product gives 3-acetamido- α -methylaltroside 2 : 4 : 6-triacetate, identical with (III). L. S. T.

Hofmann degradation of glutamine residues in gliadin. R. L. M. SYNGE (Biochem. J., 1939, 33, 671–678).—Treatment of *N*-acetylglutamine with alkaline NaOBr yields *L*- α -diaminobutyric acid (I) (50%), which may also be successively isolated from a protein digest as the phosphotungstate and di-flavinate, m.p. 239° (decomp.). Three oxalates have been obtained: (I), 0.5H₂C₂O₄ · 1.5H₂O, m.p. 211° (decomp.), (I), H₂C₂O₄, m.p. 206° (decomp.), and (I), 1.5H₂C₂O₄, m.p. 177° (decomp.). P. G. M.

Deamination of glycine in the presence of tyrosinase and *p*-cresol.—See A., 1939, III, 624.

Preparation of natural amino-acids from racemates by means of *d*-amino-acid oxidase. R. DUSCHINSKY and J. JEANNERAT (Compt. rend., 1939, 208, 1359–1361).—*dl*-Alanine in aq. LiOH at *p*_H 8.3–8.5 at 38° with *d*-amino-acid oxidase (cf. Krebs, A., 1935, 1014) in an atm. of O₂ gives *L*(+)-alanine (83.5%) $[\alpha]_D^{20}$ +14.1° in HCl, AcCO₂H, and NH₃. *dl*-Methionine similarly gives *L*(–)-methionine (68%), $[\alpha]_D^{20}$ –8° in H₂O, α -keto- γ -methylthiolbutyric acid (2 : 4-dinitrophenylhydrazones, m.p. 128°), and NH₃. The natural isomerides of valine and isoleucine are prepared similarly. J. L. D.

Methionine. II. *dl*-Methionine sulphoxide. G. TOENNIES and J. J. KOLB (J. Biol. Chem., 1939, 128, 399–405).—*dl*-Methionine sulphoxide (improved prep.) forms a *picrate*, gives no salt with HgCl₂, is quantitatively reduced by NaI in HClO₄, and oxidises cysteine to cystine. J. D. R.

Substituted ammonium sulphamates. M. J. BUTLER and L. F. AUDRIETH (J. Amer. Chem. Soc., 1939, 61, 914–915).—See A., 1939, I, 333. *Sulphamates*, NH₂·SO₃H₂B, are described, derived from the following bases *B*: NH₂Me, m.p. 91–92°; NHMe₂, m.p. 86–87°; NMe₃, m.p. 147.5–149°; NH₂Et, m.p. 65–70°; NH₂Pr^a, m.p. 67–69°; NH₂Pr^b, m.p. 74–75°; NH₂Bu^a, m.p. 107–108°; NH₂Bu^b, m.p. 138–139°; *n*-C₆H₁₁·NH₂, m.p. 128–129°; NH₂·[CH₂]₂·Pr^b, m.p. 185°; *n*-C₈H₁₇·NH₂, m.p. 109–111°; NH₂·CH₂·CH₂Et, m.p. 89–90°; (CH₂·NH₂)₂, m.p. 156–158°; NH₂·CHMe·CH₂·NH₂, m.p. 155–156°; cyclohexylamine, m.p. 157–158°; dicyclohexylamine, m.p. 160–162°; NH₂·[CH₂]₂·Ph, m.p. 183–184°; NH₂·[CH₂]₃·Ph, m.p. 104–105°.

Condensation of cyanoacetamide with formaldehyde. III. Secondary amines as catalysts. T. ENKVIST [with G. ANDERSSON] (J. pr. Chem., 1939, [ii], 158, 116–126; cf. A., 1937, II, 329, 403).—Determination of the initial rate of decrease of [CH₂O] when equimol. amounts of CH₂O and CH₂·CH₂·CO·NH₂ are mixed in PO₄^{'''}-buffered aq. solution at const. *p*_H shows that approx. the same acceleration is induced by the *sec.* amines piperidine (I), NH₂Et₂, diisomylamine, and NH(C₂H₄·OH)₂ (as hydrochlorides). Piperazine per equiv. is somewhat less active, whilst hippuric acid and guanidinoacetic acid have no appreciable effect. In presence of piperidine hydrochloride (II) at differing *p*_H the magnitude of the increase in the initial rate is approx. \propto the concn. of

(II), increases in more strongly acid solution approx. $\propto [\text{OH}']^2$, and in the less acidic region does not increase so markedly with $[\text{OH}']$. Kinetic evidence is therefore adduced that the reaction proceeds through the formation from (I) and CH_2O of an intermediate, the structure of which is discussed. Piperidinomethanol and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ yield *cyano-dipiperidinomethylacetamide*, $(\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2)_2\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$, m.p. 112° (slight decomp.) in a bath preheated to 100° . H. W.

Acetylated aldonamides. V. DEULOFEU and E. R. DE LABRIOLA (J. Amer. Chem. Soc., 1939, 61, 1110—1111).—*l*-Arabonamide, m.p. 123° , $[\alpha]_D^{25} -25.3^\circ$ in CHCl_3 , *d*-xylonamide, m.p. 112° , $[\alpha]_D^{25} +8.1^\circ$ in CHCl_3 , and *l*-rhamnonamide tetra-acetates, m.p. 115° , $[\alpha]_D^{25} -48.8^\circ$ in CHCl_3 (obtained in poor yield from the nitrile by $\text{HBr}\cdot\text{AcOH}$), *d*-mannonamide penta-acetate, m.p. 112 — 113° , $[\alpha]_D^{25} +39.1^\circ$ in CHCl_3 (not obtained from the nitrile), and *d*-galactonamide penta-acetate, m.p. 166° , $[\alpha]_D^{25} +26.4^\circ$ in CHCl_3 , are best obtained from the aldonamides by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$. Passage from a nitrile acetate to an amide acetate causes a diminution in $[\alpha]$, except in the *l*-rhamnonic series. R. S. C.

Connexion between taste and constitution of carboxylic acid hydrazides and their derivatives.

J. J. BLANKSMA and H. A. BAKELS (Rec. trav. chim., 1939, 58, 497—513; cf. A., 1938, II, 86).—Condensation of malono- (I) and succino-dihydrazide, m.p. 166° (both have a sweet taste), with aldehydes and ketones affords *malono-* and *succino-di-alkyl(aryl)idene-hydrazides* of the following [m.p. of derivative of (I) given first]: MeCHO , m.p. 188° , 250° ; EtCHO , m.p. 175° , 238° ; Pr^iCHO , m.p. 169° , 241° ; Pr^sCHO , m.p. 173° , 203° ; Bu^iCHO , m.p. 166° , 221° ; $\text{Me}\cdot[\text{CH}_2]_5\cdot\text{CHO}$, m.p. 157° , —; PhCHO , m.p. 236° , 252° ; $\text{CH}_2\text{Ph}\cdot\text{CHO}$, m.p. 170° , 228° ; 2-, m.p. 285° , 255° , and 4-hydroxy-, m.p. 202° , 240° ; 2-, m.p. 249° , 286° ; 3-, m.p. 228° , 315° , and 4-nitro-, m.p. 256° , 292° ; 2-, m.p. 229° , 269° ; 3-, m.p. 210° , 254° , and 4-chloro-, m.p. 257° , 288° ; and 4-methoxy-benzaldehyde, m.p. 222° , 235° (known). 4-hydroxy-3-methoxybenzaldehyde, m.p. 219° , —; piperonal, m.p. 221° , 268° ; vanillin, m.p. —, 209° ; furfuraldehyde, m.p. 243° , 267° , and its 5-Me, m.p. 207° , 235° , and 5- $\text{CH}_2\cdot\text{OH}$, m.p. 187° , 199° , derivatives; COMe_2 , m.p. 185° , 200° ; COMeEt , m.p. 142° , 165° ; COEt_2 , m.p. 130° , 160° ; COMePr , —, 144° ; COPr^i , 109° , 173° ; COPhMe , m.p. 220° , 274° ; COPh_2 and (I) do not react. The derivatives from COMe_2 have a bitter taste; the latter and H_2O -solubility diminish with increase in size of alkyl groups. Citric acid trihydrazide (very sweet taste) affords H_2O -insol. trihydrazides from: PhCHO , m.p. 213° ; 2-, m.p. 206° ; 3-, m.p. 185° , and 4-nitro-, m.p. 274° ; 2-, m.p. 211° , and 4-hydroxy-, m.p. 280° ; and 4-methoxy-benzaldehyde, m.p. 200° ; piperonal, m.p. 195° ; furfuraldehyde, m.p. 179° , and its 5-Me, m.p. 178° , and - $\text{CH}_2\cdot\text{OH}$, m.p. 166° , derivative; COPhMe , m.p. 182° . *o*-Phthalhydrazide, m.p. $>320^\circ$ (tasteless) [*Ac* derivative, m.p. 174° ; *N*-Me, m.p. 239° (*Ac* derivative, m.p. 140°), and *NN'*- Me_2 derivative, m.p. 175°], affords a bitter hydrazine salt. iso-, m.p. 227° , and *Tere-phthalaldihydrazide*, m.p. $>320^\circ$, afford dihydrazones with COMe_2 , m.p. 255° and 310° (faintly

bitter), PhCHO , m.p. 254° and 336° (tasteless), and COPhMe , m.p. 251° and —, respectively. 2-Hydroxymethyl- (II) and 5-nitro-2-hydroxymethyl-benzohydrazide (both bitter) afford derivatives from the following: COMe_2 , m.p. 147° (bitter) and new m.p. 185° (tasteless); PhCHO , new m.p. 152° and 196° . These are new: from 2-, m.p. 186° , 207° ; 3-, m.p. 186° , 189° , and 4-nitro-, m.p. 213° , 217° ; 2-, m.p. 182° , 207° ; 3-, m.p. 153° , 198° , and 4-chloro-benzaldehyde, m.p. 175° , 202° ; furfuraldehyde, m.p. 168° , 181° ; 5-methyl-, m.p. 183° , 161° , and 5-hydroxymethyl-furfuraldehyde (tasteless), m.p. 157° (*Ac* derivative is bitter), 166° ; piperonal, m.p. 183° , 203° . (II) and MeCHO , COPhMe , or COPr^i give (?) $(\text{CHPh}\cdot\text{N})_2$. 5-Amino-2-hydroxymethylbenzohydrazide, m.p. 147° , and its condensation product with COMe_2 , are bitter. Meconine (bitter) and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH give 5:6-dimethoxy-2-hydroxymethylbenzohydrazide (bitter) (tasteless product with COMe_2). 3-Nitro-5:6-dimethoxyphthalide and N_2H_4 afford 3-nitro-5-methoxy-6-hydrazinophthalide, m.p. 220° (tasteless derivatives with COMe_2 and PhCHO); 3-aminomeconin, however, and N_2H_4 give 3-amino-5:6-dimethoxy-2-hydroxymethylbenzohydrazide, m.p. 157° (tasteless). $\text{NHBz}\cdot\text{NH}_2$, $\text{NHBz}\cdot\text{N}\cdot\text{COMe}_2$, and $\text{NHBz}\cdot\text{N}\cdot\text{CHPh}$, are tasteless. More than one $\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ group, suitably situated, affords a sweet taste. A. T. P.

Reaction of phosphoric acid with trioxymethylene. P. PRATESI (Annali Chim. Appl., 1939, 29, 123—127).—The substance reported as Ca formaldehyde phosphate (A., 1937, III, 483) is shown to be $\text{OMe}\cdot\text{CaPO}_3$ (corresponding Hg^I salt); further attempts to prepare the former failed. The mechanism of the reaction between H_3PO_4 and trioxymethylene is discussed. F. O. H.

Hydrides of boron. XII. s-Dimethyldiborane and the methyl derivatives of borine trimethylamine. H. I. SCHLESINGER, N. W. FLODIN, and A. B. BURG (J. Amer. Chem. Soc., 1939, 61, 1078—1083; cf. A., 1939, II, 205).— $\text{B}_2\text{H}_5\text{Me}$ (prep. from BMe_3 and a large excess of B_2H_6 at 80°) and Me_2O at -80° give $\text{BH}_3\cdot\text{Me}_2\text{O}$ and *s*-dimethyldiborane, b.p. 4.9° (calc. from the v.p.), m.p. -124.9° , the reaction depending on fission and re-formation of B-B linkings and on the depression of the stability of $\text{BH}_3\cdot\text{X}$ complexes by substitution of Me in the BH_3 . The decreasing stability due to Me is shown by (a) the ease of substitution of $\text{BR}_3\cdot\text{NMe}_3$ ($\text{R} = \text{H}$ or Me) by Cl by means of HCl , (b) the series: trimethylborine trimethylamine, $\text{BMe}_3\cdot\text{NMe}_3$, 70% dissociated at 80° ; dimethylborine trimethylamine, b.p. 171.4° (calc. from the v.p.), m.p. -18.0° , stable at 68° ; methylborine trimethylamine, b.p. 176.4° (calc. from the v.p.), m.p. 0.8° , stable at 100° , and (c) the reactions: at $>68^\circ$, $2\text{BHMe}_2\cdot\text{NMe}_3 \rightarrow \text{BH}_2\text{Me}\cdot\text{NMe}_3 + \text{BMe}_3\cdot\text{NMe}_3$; and at 200° (not at 100°), $3\text{BH}_2\text{Me}\cdot\text{NMe}_3 \rightarrow 2\text{BH}_3\cdot\text{NMe}_3 + \text{BMe}_3\cdot\text{NMe}_3$. With H_2O (excess) at room temp. $(\text{BH}_2\text{Me})_2$ gives $\text{BMe}(\text{OH})_2$ and 4 H_2 . With NH_3 at -100° to -80° $(\text{BH}_2\text{Me})_2$ gives an ammoniate, $(\text{BH}_2\text{Me})_2\cdot 2\text{NH}_3$, which at 200° gives 40% of tri-*B*-methyltriborine triamine, 20% of mono- plus di-*B*-methyltriborine triamine, 4% of triborine triamine, and 2% of $\text{BMe}_2\cdot\text{NH}_2$. With NMe_3 , $(\text{BH}_2\text{Me})_2$ gives pure $\text{BH}_2\text{Me}\cdot\text{NMe}_3$. $(\text{BH}_2\text{Me})_2$

is stable for a few min. at room temp., but then rearranges to $\text{BHMe}_2\cdot\text{BH}_3$, which later decomposes partly to nearly equiv. amounts of $\text{B}_2\text{H}_5\text{Me}$ and $\text{B}_2\text{H}_3\text{Me}_2$; $(\text{BH}_2\text{Me})_2$ is absent from the final equilibrium mixture.

R. S. C.

Derivatives of monosilane. I. Reactions of chlorosilane with aliphatic amines. H. J. EMELEUS and N. MILLER (J.C.S., 1939, 819—823).—Mainly a detailed account of results already reported (A., 1939, II, 53). $\text{NMe}(\text{SiH}_3)_2$ with NaOH gives NH_2Me , Na_2SiO_3 , and H_2 , and with HCl yields NH_2Me and SiH_3Cl . $\text{NEt}(\text{SiH}_3)_2$ reacts similarly with HCl . $\text{SiH}_3\cdot\text{NMe}_3\text{Cl}$ dissociates into NMe_3 and SiHCl_3 , the reaction being irreversible owing to decomp. of SiHCl_3 into SiH_4 and SiH_2Cl_2 . V.p. of $\text{NMe}(\text{SiH}_3)_2$ and $\text{NEt}(\text{SiH}_3)_2$ are recorded. Stability of $\text{NMe}_2(\text{SiH}_3)_{4-x}\text{Cl}$ increases as x increases.

R. S. C.

Transformation of formals into halogen compounds. N. TURKIEWICZ (Ber., 1939, 72, [B], 1060—1063).—The modest yields of carbinols (and hence of halides) obtained by the process, $\text{MgRCl} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{R}\cdot\text{O}\cdot\text{MgCl} \rightarrow \text{CH}_2\text{R}\cdot\text{OH}$, are caused by the production of formals which, however, can readily be converted into carbinols, thus raising the overall yield to 91% of carbinol or 84.5% of chloride. Thus $\text{Mg cyclopentyl chloride}$ and $(\text{CH}_2\text{O})_3$ or CH_2O give *cyclopentylcarbinol* (I), b.p. 161—163° (40%), *dicyclopentyl* (12.5%), and *dicyclopentylmethyl formal*, b.p. 145°/9 mm. (40.5%), which is converted into (I) by boiling EtOH-HCl . Rapid addition of (I) to PCl_5 under light petroleum gives *cyclopentylmethyl chloride*. Similarly, *octadecyl chloride* affords a mixture of *n*-octadecane and *octadecene*, *n*-nonadecanol, m.p. 61.5°, and *dinonadecyl formal*, b.p. 280°/0.3 mm., m.p. 60°. *Nonadecyl chloride* has b.p. 164—167°/0.3 mm. Analogously *dodecyl chloride* afforded *olefines*, *tridecanol*, b.p. 152°/14 mm., m.p. 30.5°, *tetracosane*, and *ditridecyl formal*, which is converted by an excess of PBr_5 in hot C_6H_6 into *tridecyl bromide*, b.p. 162°/16 mm.

H. W.

Relative reactivities of magnesium methyl chloride and magnesium dimethyl. G. F. WRIGHT (J. Amer. Chem. Soc., 1939, 61, 1152—1156).— MgMe_2 in dioxan reacts much more readily with the OH than with the CO of COPh-CHPh-OH (I); a complex, $\text{CHPh}\cdot\text{O}\cdot\text{Mg}$, is probably formed. By interaction with (I), COPhMe , $\text{CH}_2\text{Ph-COPh}$, and COPh-CHPh_2 , it is shown that MgMe_2 is less reactive towards enolisable CO than is MgMeHal .

Carbonation of organo-magnesium compounds and the accompanying secondary reactions in the aliphatic series. M. TUOT (Compt. rend., 1939, 208, 1026—1028).—Carbonation of Mg derivatives of Pr^nBr , Pr^iBr , Bu^nBr , and Bu^iBr at -15° to -20° affords the corresponding acids (90—100%). A large excess of MgRBr and prolonged heating at 40° gives, with Pr^nBr and Bu^nBr , <10% of the corresponding acid, the ketone obtained by interaction of 2MgRBr with CO_2 , and a *tert.* alcohol due to the further action of MgRBr on the ketone (cf. A., 1938, II, 257), also primary and *sec.* alcohols

and an unsaturated hydrocarbon. Pr^iBr and Bu^iBr give similar products, but no *tert.* alcohol is formed. The reaction mechanisms are described. The saturated hydrocarbons to be expected from the reaction mechanism proposed by Mousseron and Granger (A., 1937, II, 449) are not produced (cf. A., 1939, II, 102).

J. L. D.

Organic compounds of gold. VII. Methyl and ethyl compounds. F. H. BRAIN and C. S. GIBSON (J.C.S., 1939, 762—767; cf. A., 1936, 618).— Me and Et derivatives of Au have been prepared. Au^{III} has little, if any, tendency to become 5-covalent. *Pyridinotrichlorogold* and MgMeI in $\text{C}_5\text{H}_5\text{N}$ at $<0^\circ$ give 21% of *dimethyliodogold* (I), $(\text{Me}_2\text{AuI})_2$, m.p. 78.5° (liquid explosive), the mol. wt. of which is found by cryoscopy in C_6H_6 or CHBr_3 , although its solutions therein are unstable at room temp. With alkali in EtOH , (I) gives a Au mirror. With $(\text{CH}_2\cdot\text{NH}_2)_2$ in EtOH , (I) gives *ethylenediaminodimethylgold iodide*, $[\text{Me}_2\text{Au}(\text{CH}_2\cdot\text{NH}_2)_2]\text{I}$, m.p. 168° (decomp.), reconverted by HCl into (I), but converted by HI into *ethylenediaminotetramethyldiiodogold* (III), $(\text{CH}_2\cdot\text{NH}_2)_4\text{AuMe}_2\text{I}_2$, decomp. when heated. With $(\text{CH}_2\text{Ph})_2\text{S}$, (I) gives *dibenzylsulphidodimethyliodogold*, $(\text{CH}_2\text{Ph})_2\text{S}\rightarrow\text{AuMe}_2\text{I}$, m.p. 77—78° (decomp.), and with Ti acetylacetone yields *dimethylgoldacetylacetone*, $\text{Me}_2\text{Au}\begin{matrix} \text{CO}\cdot\text{CMe} \\ \diagup \quad \diagdown \\ \text{O}=\text{CMe} \end{matrix}\text{CH}$, m.p. 84°,

less sensitive to light than is the Et analogue and converted by HBr-EtOH into *dimethylbromogold* (IV) [formula as (I)], m.p. 68—69° (decomp.). With Br in CCl_4 (IV) gives *methylidibromogold*, $(\text{Me}_2\text{AuBr})_2$; *cryst.* $\text{Au}_2\text{Et}_4\text{Br}_2$ does not react with Et_3S , but yields normally *dibenzylsulphidodiethylbromogold*, m.p. 91°, converted by $(\text{CH}_2\cdot\text{NH}_2)_2$ into *ethylenediaminodiethylgold*. ($\beta\beta'$ -*Diaminodiethyl ether-tetraethylidibromodigold*, $\text{O}[(\text{CH}_2)_2\cdot\text{NH}_2]\rightarrow\text{AuEt}_2\text{Br}_2$, m.p. 87° (decomp.), and *NN-diethylethylenediaminotetraethylidibromodigold* (V), $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NEt}_2\rightarrow\text{AuEt}_2\text{Br}_2$, m.p. 83.5° (decomp.), are readily obtained, but the Et analogue of (III) was not formed. *NN-Diethylethylenediaminodiethylgold bromide* (VI), $[\text{Et}_2\text{Au}(\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NEt}_2)]\text{Br}$, hygroscopic, m.p. $\sim 26^\circ$, is prepared; it is sol. in H_2O and dissociates therein. However, in C_6H_6 , CHCl_3 , etc. it is a non-electrolyte, probably existing as $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2\rightarrow\text{AuEt}_2\text{Br}$, the change being reversible. It is considerably associated in C_6H_6 , possibly as $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2\rightarrow\text{AuEt}_2\text{Br}\rightarrow\text{AuEt}_2(\leftarrow\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NEt}_2)\text{Br}\rightarrow\text{AuEt}_2$ etc.; the Au , except in the end units, would then be 5-covalent. With $\text{C}_5\text{H}_5\text{N}$ (V) gives (VI). 2:2'-*Dipyridyl* and $\text{Au}_2\text{Et}_4\text{Br}_2$ give 2:2'-*dipyridyltetraethylidibromodigold*, $(\text{C}_5\text{H}_5\text{N})\rightarrow\text{AuEt}_2\text{Br}_2$, m.p. 169°, readily converted into (VI).

R. S. C.

Isomerisation of alkylcyclopentanes. H. PINES and V. N. IPATIEV (J. Amer. Chem. Soc., 1939, 61, 1076—1077).—With AlCl_3 and a trace of H_2O at 50° *ethylcyclopentane* (I), b.p. 103.6°, gives *methylcyclohexane*; *n*- (II), b.p. 130.7°, and *iso-propylcyclopentane* (III), b.p. 126.8°, give 1:3-dimethylcyclohexane; *n*- (IV), b.p. 156.8°, *sec.*- (V), b.p. 154.6°, and *tert.*-butylcyclopentane, b.p. 145.2°, give 1:3:5-

trimethylcyclohexane. Formation of polymethylcyclopentanes probably precedes ring-enlargement. The structure of the products is proved by dehydrogenation (7% Pt-Al₂O₃; 240°), bromination, and/or nitration. (I), (II), and (IV) are prepared by treating cyclopentanone with MgAlkHal, dehydrating by passage over activated Al₂O₃ at 345°, and hydrogenating in presence of Ni at 100°/100 atm. (III) and (V) are prepared by treating cyclopentadiene with COMe₂ or COMeEt, respectively, and NaOEt-EtOH at 40° and hydrogenating (Ni) the resulting dialkylfulvene at 125°/100 atm.

R. S. C.

Synthesis of homologues of phenylcyclopentane. J. I. DENISENKO and A. D. NABER (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1025—1032).—*ω*-Chloro-*n*-amyl- and -hexyl-benzene with Mg and cyclopentanone yield respectively 1-*ω*-phenyl-*n*-amyl-, b.p. 168—169°/3 mm., and -hexyl-cyclopentanol, b.p. 181—182°/3 mm., dehydrated (H₂C₂O₄ in H₂O) to the -Δ¹-cyclopentenes, b.p. 157—158°/3 mm. and 159—160°/2 mm., respectively, reduced (Pt-black) to the -cyclopentanes, b.p. 304—305°/748 mm. and 315—317°/749 mm., respectively. 1-*ω*-Phenyl-ethyl- and -propyl-cyclopentanol with anhyd. H₂C₂O₄ at 110—135° yield cyclopentanotetrahydronaphthalene and octahydrophenanthrene, respectively. The properties of Ph·[CH₂]_{*n*}·C₆H₅ (*n* = 0—6) and related compounds are tabulated.

A. Li.

Multiplanar structure of the methylcyclohexane ring. D. M. COWAN, G. H. JEFFERY, and A. I. VOGEL (Chem. and Ind., 1939, 559; cf. A., 1938, II, 268, 354, 436).—The methylcyclohexane *B* obtained by the thermal decomp. of 2-methylcyclohexanone-semicarbazone in presence of NaOEt has b.p. 100.4°/763 mm. (vals of *d* and *n* quoted in all cases) which changes after several days. The hydrocarbon from the 4-Me compound has b.p. 100.5°/764 mm., changing to 100.4°/758 mm. after several days. The original form *B'* had b.p. 100.2—100.4°/768 mm. The prep. of form *B'* by Clemmensen reduction of 2-, 3-, and 4-methylcyclohexanones is announced. The original form *A* is now regarded as slightly impure *B'*. It is claimed that the two Sachse forms of methylcyclohexane may have been proved capable of independent existence.

H. W.

Reaction of cyclopentene with sulphur dioxide solution. O. PRIPIK (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1097—1104).—cyclopentene (both synthetic and that obtained from cracked petroleum) forms a sulphone with SO₂ solution. Positive and negative catalysts for the reaction have been found. A sulphone reagent is described for the determination of active groups in the mol., and of the liability of org. compounds to oxidation, and has been applied to the oxidation of petroleum products.

A. Li.

Simultaneous dehydrogenation-hydrogenation of cyclohexene in presence of nickel. B. B. CORSON and V. N. IPATIEV (J. Amer. Chem. Soc., 1939, 61, 1056—1057).—Ni-kieselguhr (65 : 35) catalyses change of cyclohexene (3 mols.) at 125—200° into cyclohexane (2 mols.) and C₆H₆ (1. mol.), but with higher temp. (up to 400°) the amount of C₆H₆ increases. Small amounts of H₂ and CH₄ are also formed, the

amounts depending on the temp. and whether the steel autoclave has or has not a glass liner.

R. S. C.

Addition of hydrogen to aromatic hydrocarbons by the action of ammonia complexes of lithium, strontium, and barium. III. B. A. KAZANSKI and N. F. GLUSCHNEV (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1061—1064).—C₆H₆ and PhMe are reduced by Li in NH₃, or by Sr or Ba ammoniate, to H₂- and H₄-derivatives.

A. Li.

Dehydrogenation of cyclooctene. S. GOLD-WASSER and H. S. TAYLOR (J. Amer. Chem. Soc., 1939, 61, 1260—1263).—An apparatus for studying the catalytic behaviour of semi-micro-quantities of volatile compounds is described. In presence of Cr (prep. from Cr₂O₃ gel by H₂) at 400° cyclooctene gives 1 H₂ and 1 part each of cyclooctane and styrene. At 425—500°, however, loss of H₂ is more rapid than hydrogenation; 2.7 H₂ are liberated and the product contains 6—8% of cyclooctane and 92—94% of styrene. These proportions are calc. (concordantly) from the H₂ evolved, *d* and I val. of the product. Willstätter's reputed cyclooctatetraene (cf. A., 1912, i, 17; 1913, i, 348) was probably styrene, with which its properties accord.

R. S. C.

Contact changes of phenylcyclopentane homologues. J. I. DENISENKO (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1019—1024).—With Pt-C at 300—310° in excess of H₂, cyclopentylphenyl-ethane (I) and -propane (II) give mixtures containing heptyl- and octyl-benzene respectively. With Pt-C at 310—315° in an inert gas, (I) and (II) yield 4 : 5-benzoinane and phenanthrene respectively.

A. Li.

***α*-cyclopentyl-*δ*-phenylbutane and its transformations.** J. I. DENISENKO and A. D. NABER (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1015—1018).—*δ*-Chloro-*n*-butylbenzene with Mg and cyclopentanone yields 1-*δ*-phenyl-*n*-butyl-cyclopentanol, b.p. 155—156°/3 mm., dehydrated (H₂C₂O₄·2H₂O) to the -Δ¹-cyclopentene, b.p. 146—147°/6 mm., which with H₂-Pt-black at room temp. yields the -cyclopentane (I), b.p. 289—290°/754 mm. (I) is reduced (H₂, Pt-C at 230°) to *α*-cyclopentyl-*δ*-cyclohexyl-*n*-butane, b.p. 284.5—286°/745.1 mm., dehydrogenated (Pt-C at 280°) to (I).

A. Li.

Hydrogenation of certain homologues of benzene under pressure. II. M. K. DJAKOVA and A. V. LOZOVOR (J. Gen. Chem. Russ., 1939, 9, 26—32).—Ph·[CH₂]₂·Br and Pr^αBr or *α*-bromo-*n*-hexane yield (Wurtz) *n*-amyl- or *n*-octyl-benzene, respectively. The following are obtained by hydrogenation of the appropriate alkylbenzene (Ni-Al₂O₃ catalyst at 160—170°/50—70 atm.): *n*-butyl-, *n*-amyl-, isoamyl-, 2- and 4-methyl-*n*-propyl-, and *n*-octyl-cyclohexane, b.p. 117—119°/11 mm.; hydrindene similarly gives octahydroindene.

R. T.

Formation of intermediate compounds in hydrocarbon syntheses by the Friedel and Crafts reaction. Preparation of *s*-trialkylbenzenes. J. F. NORRIS and D. RUBINSTEIN (J. Amer. Chem. Soc., 1939, 61, 1163—1170).—Passage of HBr into PhMe + AlBr₃ gives an oily compound, Al₂Br₆·6PhMe, decomp. in *p*-C₆H₄Cl₂ (mol. wt.

at the f.p.) or when kept at 10—11 mm. into PhMe and $\text{Al}_2\text{Br}_6 \cdot \text{PhMe}$. When aromatic hydrocarbons are alkylated (AlkHal) in presence of 1 Al_2Cl_6 or Al_2Br_6 per mol. of hydrocarbon, very high yields of *m*-derivatives are obtained; e.g., with Al_2Cl_6 , C_6H_6 and EtBr give 85—90% of *s*- $\text{C}_6\text{H}_3\text{Et}_3$, PhMe gives 85% of 1 : 3 : 5- $\text{C}_6\text{H}_3\text{MeEt}_3$, and crude *m*-xylene gives 50% of *s*- $\text{C}_6\text{H}_3\text{Me}_3$ (87% of the total Me_3 derivatives). Using AlCl_3 , C_6H_6 and MeBr at 0° give mainly ψ -cumene, but at the b.p. mainly *s*- $\text{C}_6\text{H}_3\text{Me}_3$. At 0° PhMe and MeCl give 27.3% of *m*- and 53.5% of *o*-xylene, but at 106° 98.2% of *m*- and 1.8% of *o*-xylene. With AlCl_3 at 55° (10 min.) *o*-xylene gives 18.7% and *p*-xylene gives 64.3% of *m*-xylene. A cryoscopic method of analysing xylene mixtures is outlined. R. S. C.

Polymethylbenzenes. XXIV. Jacobsen reaction. VI. Trimethylethylbenzenes. L. I. SMITH and M. A. KIESS (J. Amer. Chem. Soc., 1939, 61, 989—996; cf. A., 1937, II, 372).—When 5-ethyl- ψ -cumene (I) or, less readily, ethylmesitylene (II) is sulphated by 10% oleum at <40° and then heated therein at 60—70°, rearrangement occurs; hydrolysis gives largely (41.7 and 57.5%, respectively) 3-ethyl- ψ -cumene (III), which is unchanged by this treatment. (I) yields also ψ -cumene (6.7%), 4-ethyl-*m*-xylene (IV) (14.4%), prehnitene (V) (11.2%), and much tar, including a small amount of a (?) *hexa-alkylbenzene*, m.p. 173—175°. (II) yields also mesitylene (6.7%), 2-ethyl-*m*-xylene (VI) (15.9%), (V) (16.6%), and much tar, including a substance (C 89.5, H 10.4%), m.p. 185—186°. Formation of (V) indicates a novel mode of reaction. (I) shaken with 10% oleum for 5 min. gives 5-ethyl- ψ -cumenesulphonic acid, m.p. 72—73° (lit. 70—72°) [amide, m.p. 97—98° (lit. 86° and 153°); anilide, m.p. 110—111°], converted by $\text{Br-H}_2\text{O}$ into 3 : 6-dibromo-5-ethyl- ψ -cumene, m.p. 60—61° (lit. 218°) [also obtained direct from (I) by Br-AcOH]. By Smith's method, (I) gives the 3 : 6-(NO_2)₂-derivative, m.p. 87—88°, reduced by $\text{SnCl}_2\text{-HCl}$ to the 3 : 6-(NH_2)₂-derivative, m.p. 87—88° (*stannichloride*), which with $\text{FeCl}_3\text{-HCl}$ gives trimethylethylbenzoquinone, m.p. 43°. Conc. H_2SO_4 converts (III) into 3-ethyl- ψ -cumenesulphonic acid, m.p. 62—64° (*amide*, m.p. 154°; *anilide*, m.p. 118—119°). (IV), b.p. 85°/25 mm., gives a (NO_2)₃, m.p. 127.5—129°, and a Br_3 -derivative, m.p. 94—95° (lit. 127°), and is oxidised to 1 : 2 : 4- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$. Oxidation of (VI), b.p. 80—83°/24 mm. [(NO_2)₃-derivative, m.p. 181°], gives 1 : 2 : 3- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$. The mixture of 2- and 4-bromo-*m*-xylene, obtained directly from *m*-xylene by Br at 0°, gives a Grignard reagent, which with Et_2SO_4 in Et_2O yields (IV) and (VI), separated as (NO_2)₃-derivatives. By methods given above, (II) yields ethylmesitylenesulphonic acid, m.p. 78—80° (*anilide*, m.p. 123—124°; *amide*, m.p. 131—133°), 4 : 6-dibromo-, m.p. 59°, 4 : 6-dinitro-, m.p. 111° (lit. 123°), and 4 : 6-diamino-ethylmesitylene, m.p. 79—80°, and with fuming $\text{HNO}_3\text{-H}_2\text{SO}_4$ yields (?) 1 : 2 : 4 : 3 : 5 : 6- $\text{C}_6\text{Me}_2\text{Et}(\text{NO}_2)_3$, m.p. 123°. Clemmensen reduction of crude aceto-*p*-xylene gives ethyl-*p*-xylene [(NO_2)₃-derivative, m.p. 127—128° (lit. 129°)]. R. S. C.

Electrolytic reduction of nitrobenzene in liquid ammonia. H. SHIBA, T. INOUE, and R. MIYASAKA

(Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 35, 455—461).—The electrolytic reduction of PhNO_2 in liquid NH_3 solutions of NH_4Cl and NaCl has been investigated using an Al anode, a Ni cathode, and an asbestos diaphragm. With a 0.0001M. solution of PhNO_2 and 0.1M- NH_4Cl or NaCl the efficiency of reduction with NaCl was > in NH_4Cl . The nature of the reduction products was obtained by comparison of the absorption spectrum with that of the pure compounds. For this purpose the absorption spectra of PhNO_2 , PhNO , NPh-OH , NH_2Ph , PhNO:NPh , (NPh)₂, (NHPh)₂ and benzidine in liquid NH_3 were determined. The following results were obtained by electrolysis in NH_4Cl in liquid NH_3 : $\text{PhNO}_2 \rightarrow \text{PhNO}$; PhNO unchanged; NPh-OH unchanged; $\text{PhNO:NPh} \rightarrow (\text{NHPh})_2$; (NPh)₂ \rightarrow (NHPh)₂. With NaCl in liquid NH_3 , PhNO_2 , PhNO , or $\text{NPh-OH} \rightarrow \text{PhN:N-ONa}$ or NPhNa-ONa ; $\text{PhNO:NPh} \rightarrow (\text{NPh})_2$; (NPh)₂ \rightarrow (NHPh)₂. A. J. M.

Kinetics of chain polymerisation. V, VI.—See A., 1939, I, 375.

Diarylmethane derivatives. V. Derivatives of bis-(2 : 4 : 6-triethylphenyl)methane. W. T. NAUTA and D. MULDER (Rec. trav. chim., 1939, 58, 514—520; cf. A., 1939, II, 103).— $\text{s-C}_6\text{H}_3\text{Et}_3$ (I) (prep. from C_6H_6 , C_2H_4 , and AlCl_3 at 60—80°) and Br-CHCl_3 (no Fe) give 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Et}_3\text{Br}$, converted (Grignard method) into 2 : 4 : 6 : 1- $\text{C}_6\text{H}_2\text{Et}_3\text{CO}_2\text{H}$, the chloride of which with (I), AlCl_3 , and CS_2 at 65° affords bis-(2 : 4 : 6-triethylphenyl) ketone, m.p. 79—80°, reduced by Na-Hg in EtOH to the carbinol, m.p. 27—28°, and thence converted by $\text{HCl-C}_6\text{H}_6$ into the carbinyl chloride (II), m.p. 36—37°, and some bis-(2 : 4 : 6-triethylphenyl)methane, m.p. 71—72°. The latter is also obtained from (I) and (CH_2O)₃ in $\text{AcOH-H}_2\text{SO}_4$ at room temp. (II) and $\text{AgOAc-Et}_2\text{O}$ or KOH-MeOH give bis-(2 : 4 : 6-triethylphenyl)carbinyl acetate, b.p. 167—168°/0.75 mm., or Me ether, b.p. 169°/1 mm., respectively.

A. T. P.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. XII. Cathodic reduction of $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-*p*-bromophenylethane. K. BRAND and D. KRÜCKE-AMELUNG (Ber., 1939, 72, [B], 1029—1035; cf. A., 1930, 1285).— PhBr is converted by $\text{CCl}_3\text{-CHO}$ or $\text{CCl}_3\text{-CH(OH)}_2$ and fuming H_2SO_4 into $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-*p*-bromophenylethane (I), m.p. 144°, the structure of which is established by its transformation by boiling KOH-EtOH or, preferably, NaOBu in BuOH into $\beta\beta$ -dichloro- $\alpha\alpha$ -di-*p*-bromophenylethylene, m.p. 123.5°, which is oxidised by CrO_3 in $\text{AcOH-H}_2\text{SO}_4$ to $\text{CO(C}_6\text{H}_4\text{Br)}_2$ with a very little *p*- $\text{C}_6\text{H}_4\text{Br-CO}_2\text{H}$. Cathodic reduction (Pb) of (I) in HCl-EtOH affords $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- Δ^8 -butinene (II), m.p. 198.5°, but much (I) remains unattacked since (II) forms a protective coating on the electrode. The difficulty is obviated by the use of dioxan (or exluan)- MeOH-HCl . In addition there are obtained not inconsiderable amounts of $\beta\beta$ -dichloro- $\alpha\alpha$ -di-*p*-bromophenylethane (III), m.p. 133—134° (converted by KOH-EtOH into β -chloro- $\alpha\alpha$ -di-*p*-bromophenylethylene, m.p. 107—108°), and (after treatment with KOH) very

small quantities of $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene, m.p. 299°. CrO_3 in AcOH smoothly oxidises (II) to CO_2 and $\text{CO}(\text{C}_6\text{H}_4\text{Br}-p)_2$. It is almost quantitatively transformed by boiling the solution in EtOH or, preferably, amyl alcohol with NaOEt into $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 265–266°, which, like (II), is not reduced by Zn dust in boiling AcOH . Cathodic reduction of (I) at Cu in presence of ZnCl_2 gives (III), $\beta\beta\gamma\gamma$ -tetrachloro- $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenylbutane, and $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- Δ^{β} -butene. H. W.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. XIII.

$\alpha\alpha\delta\delta$ -Tetra-*p*-bromophenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene. K. BRAND and D. KRÜCKE-AMELUNG (Ber., 1939, 72, [B], 1036–1047).—Examination of CaCO_3 -Pd catalysts which have functioned irregularly in this work discloses the presence of considerable amounts of uncoloured calcite crystals in the inactive material and of brown aragonite crystals in the active compounds. Since even the brown material is not invariably useful, recourse is taken to a ZnO -Pd catalyst. Catalytic reduction of $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -di-*p*-bromophenylethane (I) at 65° in EtOH , exluan-06, or pure $\text{C}_2\text{H}_5\text{N}$ yields a difficultly separable mixture of $\beta\beta\gamma\gamma$ -tetrachloro- $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenylbutane (II), m.p. 299° [also + $2\text{C}_6\text{H}_5$, + 2EtOAc , and + 1.5 (?) CHCl_3], and $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- Δ^{β} -butene (III), m.p. 278.5–280°. It is therefore preferable to reduce (I) in exluan-06 mainly to (II), which is converted by Zn dust in exluan-05 into (III) and its diastereomeric form (IV), m.p. 192° after softening at 187–188°. (III) is reduced by Zn dust and AcOH to $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- Δ^{β} -butinene (V), m.p. 198.5°. (III) or (IV) is transformed by NaOEt in EtOH -amyl alcohol into $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenyl- $\Delta^{\alpha\beta\gamma}$ -butatriene (VI), m.p. 299° (decomp.), which on exposure to sunlight passes into a compound, m.p. 336.5° after darkening at 326°. Oxidation (KMnO_4 in COMe_2 containing MgSO_4) of (VI) affords $\text{CO}(\text{C}_6\text{H}_4\text{Br}-p)_2$ whilst reduction (Zn dust in AcOH) leads to (V). (VI) is slowly converted by AcOH saturated with HCl at 400° into chloro- $\alpha\alpha\delta\delta$ -tetra-*p*-bromophenylbutadiene, m.p. 161°, or under somewhat different conditions, into 6-bromo-3-*p*-bromophenyl-1-di-*p*-bromophenylmethyleneindene, m.p. 265°. H. W.

Palladous chloride as a dehydrogenating agent. G. W. COOKE and J. M. GULLAND (J.C.S., 1939, 872–873).—Tetrahydronaphthalene and 2% aq. PdCl_2 (in least amount of HCl to give solution), refluxed for 33 hr., afford C_{10}H_8 . Decahydronaphthalene similarly gives no C_{10}H_8 (odour only detected at 200° in a sealed tube). cycloHexanol affords PhOH . Tetrahydrocarbazole yields carbazole. Tetrahydro-quinoline and isoquinoline, using more HCl and adjusting p_H val., give quinoline and isoquinoline, respectively; 2-methyltetrahydroisoquinoline similarly affords 2-methyl-1:2-dihydroisoquinoline. PhMe (excess) affords BzOH ; *o*-cresol (p_H adjusted) gives *o*- $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ and *o*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, the latter being obtained also from 2-methylcyclohexanol. No product is isolated from $(\text{CH}_2\text{Ph})_2$, COMeEt

(complex formation), cyclohexane (very stable), stilbazole (complex salt), or cholesterol (very slow oxidation). Addition of org. solvents does not increase efficiency of reaction. A. T. P.

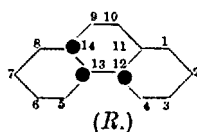
Separation of hydrocarbons of high mol. wt. by adsorption on silica gel. C. B. WILLINGHAM (J. Res. Nat. Bur. Stand., 1939, 22, 321–327).—Filtration through SiO_2 gel completely removes small amounts of ϵ -(5:6:7:8-tetrahydro- β -naphthyl)docosane (I) from ϵ -(decahydro- β -naphthyl)docosane (II), and *n*-dotriacontane (III) from α -*p*-diphenylloctadecane (IV). A partial separation of (IV) from (I) was effected, but not of (III) from (II). The preferential adsorptions of the more aromatic constituent of the first three of these mixtures were respectively 1.8, 3.3, and 0.8 g. per 20 g. of SiO_2 gel. W. A. R.

Isomeric changes in cyclic hydrocarbons observed when trying to realise a triple linking in a ring. V. I. NIKITIN (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 1265–1276).—1-Ketotetrahydronaphthalene on successive treatment with PCl_5 , KOH , and Br yields 4-chloro-3:4-dibromo-1:2:3:4-tetrahydronaphthalene, which is unstable and gives 3:4-dibromo-1:2-dihydronaphthalene (I) (by loss of HCl) and 2- $\text{C}_{10}\text{H}_7\text{Cl}$ (loss of 2HBr). (I) with Na yields C_{10}H_8 . A. LI.

Polymerisation of α -vinylnaphthalene derivatives. S. ZONIS (J. Gen. Chem. Russ., 1939, 9, 119–125).— COMePr^a and $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ in Et_2O yield β -1-naphthylpentan- β -ol, m.p. 65–66°, whilst with COMePr^b β -1-naphthyl- γ -methylbutan- β -ol, b.p. 177–179°/10–11 mm., is obtained. The alcohols are dehydrated by activated clay at 140–150° to β -1-naphthyl- Δ^{β} -pentene (I), b.p. 158–160°/20 mm., and β -1-naphthyl- γ -methyl- Δ^{β} -butene (II), b.p. 165–166°/23 mm., respectively. When the hydrocarbons $\text{CHR}:\text{CHR}'$ and $\text{CRR}':\text{CH}_2$ ($\text{R} = \alpha\text{-C}_{10}\text{H}_7$, $\text{R}' = \text{Me}$) were left in contact with fluoridin or BzO_2H for 3–8 months at room temp., dimers were formed; under these conditions (I) and (II) do not polymerise.

R. T.

Fused carbon rings. XVI. Stereoisomerism of the perhydrophenanthrenes; preliminary investigations. R. P. LINSTAD and A. L. WALPOLE (J.C.S., 1939, 842–850).—Nomenclature and structural representation of the six inactive forms of perhydrophenanthrene, 4 racemic, viz., *cis-syn-trans* (R), *cis-anti-cis*, *cis-anti-trans*, *trans-anti-trans*, and 2 meso-, viz., *cis-syn-cis* and *trans-syn-trans*, are discussed. Hexagons represent fully reduced cyclohexane rings. The black dots indicate H atoms above the general plane of the mol. Di-1-hydroxycyclohexylacetylene is dehydrated (40% H_2SO_4 is preferable to KHSO_4) to di- Δ^1 -cyclohexenylacetylene, which with HCO_2H affords 9-ketododecahydraphenanthrenes, m.p. 93–94° (I) and m.p. 38–39° (b.p. 146–147°/5 mm.) (II) (cf. Marvel *et al.*, A., 1938, II, 48), purified through the respective oximes, m.p. 157–158° and 183–184° (prepared from $\text{NH}_2\text{OH}\cdot\text{HCl}$ - NaOAc -aq. EtOH); the respective semicarbazones have m.p. 232° and 227–228°. A third 9-ketododecahydraphenanthrene, m.p. 88°



(III) (modified method of prep. of Rapson and Robinson, A., 1935, 1498), gives an oxime, m.p. 202°. (I) and (II) differ solely in the position of the double linking; in one it is 8 : 14 and in the other is 13 : 14. (I) or (II) react slowly with ICl in CHCl_3 -EtOH, i.e., double linkings are in $\alpha\beta$ -positions, proved by ultra-violet absorption spectra. (III), also with an $\alpha\beta$ -double linking, is probably a *trans*¹³- Δ^{10} -form. No isomerisation is noted with (I) or (II) at 200° in N_2 , with piperidine in N_2 at 100° or 200°, or with *n*-Na *tert*-amyloxide at room temp. or 100°; (III) generally yields viscous material. (I) or (II) is hydrogenated (Pd-C in EtOH, or Adams' catalyst in AcOH) to 9-ketoperhydrophenanthrene, form A, m.p. 51° (mainly) (oxime, m.p. 163—164°; semicarbazone, m.p. 187°), and a form B, b.p. 128°/2 mm. (oxime, m.p. 184—185°; semicarbazone, m.p. 182—183°), which are *trans*¹³- and *cis*¹³-forms, respectively, and otherwise of identical configuration. A is unchanged at 250° in N_2 for 1 hr., or by boiling with NaNH_2 - C_6H_6 . B is converted into A at 280° in N_2 . Hydrogenation of (III) affords solely a *trans*¹³-9-ketoperhydrophenanthrene, form C, m.p. 47—48° (oxime, m.p. 227—228°), unchanged by NaNH_2 - C_6H_6 . (I) or (II) and Na-EtOH give mixtures, oxidised by CrO_3 -AcOH to A. (III) similarly gives 9-hydroxyperhydrophenanthrene, m.p. 119°, oxidised to C. (I) or (II) is reduced (Clemmensen) to dodecahydrophenanthrenes, b.p. 121—122°/12 mm. or 116°/9 mm. (double linking migration is indicated as either form with amyl nitrite gives a pale blue nitrosochloride, m.p. 191°), and physical properties show that they differ, or at least contain considerable amounts of different isomerides. Either form and Pd-C at 330—340° give phenanthrene. A is reduced (Clemmensen) to a product, purified by K at 210° and then with H_2SO_4 -oleum, to give a perhydrophenanthrene, b.p. 140—140.5°/18 mm.; C similarly gives an isomeride, m.p. 10°, which is probably homogeneous. A and MgMeI give a *tert*-alcohol, dehydrated by repeated distillation at 40 mm. with a little I (followed by K at 210°) to 9-methyl-dodecahydrophenanthrene, b.p. 140°/15.5 mm., dehydrogenated (Pd-C) in the vapour phase at 330° to 9-methylphenanthrene (picrate, m.p. 148—149°).

A. T. P.

Bisdiphenylene-ethylene series. C. COURTOT and J. KROUSTEIN (Compt. rend., 1939, 208, 1230—1233; cf. Korczyński *et al.*, A., 1927, 347).—7-Nitrofluorene with Br in PhNO_2 at 110—170° gives a red compound (I), m.p. >450° [which with $\text{K}_2\text{Cr}_2\text{O}_7$ in boiling 20% H_2SO_4 (40 hr.) gives 2-bromo-7-nitrofluorenone (II), m.p. 230° (cf. A., 1927, 234)], and with Br (2 mols.) at 150° 2 : 9-dibromo-7-nitrofluorene (III), m.p. 206° [oxidised to (II), and with Zn-aq. NH_3 gives 2-bromo-7-aminofluorene]. (III) with Br (1 mol.) in PhNO_2 at 160° gives (60%) 2 : 2'-dibromo-7 : 7'-dinitrobisdiphenylene-ethylene [? (I)] (cf. Bergmann *et al.*, A., 1933, 152). A suspension of (I) in PhNO_2 with excess of Br at 160°, affords a colourless compound, $\text{C}_{28}\text{H}_{12}\text{O}_4\text{N}_2\text{Br}_4$, which decomposes in hot tetralin or PhNO_2 or at 250° to give (I). 2 : 7-Dinitrofluorene with Br (2 mols.) in PhNO_2 gives 2 : 2' : 7'-tetranitrobisdiphenylene-ethylene, m.p. >450° (cf. Hughes and Kuriyan, A., 1936, 62), oxidised to 2 : 7-dinitrofluorenone. J. L. D.

Dehydrogenation. III. S. C. SEN-GUPTA (J. Indian Chem. Soc., 1939, 16, 89—94; cf. A., 1939, II, 148).—Hydrindene (I), $(\text{-CH}_2\text{-CO})_2\text{O}$, and AlCl_3 in PhNO_2 give γ -keto- γ -5-hydrindyl-*n*-butyric acid, m.p. 123—124°, oxidised by alkaline KMnO_4 to 1 : 2 : 4- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ (II) and reduced by Zn-Hg-HCl to γ -5-hydrindyl-*n*-butyric acid, m.p. 56°, b.p. 190—192°/6 mm., which with 85% H_2SO_4 at 100° gives 1-keto-6 : 7-trimethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (III), b.p. 167°/6 mm. The structure of (III) is proved by oxidation (alkaline KMnO_4) to 1 : 2 : 4 : 5- $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ (IV). Clemmensen reduction of (I) affords 6 : 7-trimethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (V), b.p. 125—126°/6 mm. *as*-Dimethylsuccinic anhydride, (I), and AlCl_3 give similarly γ -keto- γ -5-hydrindyl- $\alpha\alpha$ -dimethyl-*n*-butyric acid, m.p. 139—140° (*Me* ester, b.p. 190—191°/6 mm.) [oxidised to (II)], and thence γ -5-hydrindyl- $\alpha\alpha$ -dimethyl-*n*-butyric acid, m.p. 82—83°, 1-keto-2 : 2-dimethyl-6 : 7-trimethylene-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 170°/10 mm. [oxidised to (IV)], and 2 : 2-dimethyl-6 : 7-trimethylene-1 : 2 : 3 : 4-tetrahydronaphthalene (VI), m.p. 82°. The C_5 -ring survives Se-dehydrogenation at 300—320°, for (V) gives 5 : 6-benzhydrindene, m.p. 94° (*picrate*, m.p. 120—121°), and (VI) gives 2-methyl-6 : 7-trimethylenenaphthalene, m.p. 104° (*picrate*, m.p. 107—108°). R. S. C.

Catalytic oxidation and preparation of hexahydrobenzylamine. I. I. LENARSKI (J. Gen. Chem. Russ., 1939, 9, 99—103).— NH_3 and hexahydrobenzyl alcohol passed through a layer of Ni-Al catalyst at 185° give hexahydrobenzylamine (I) in 65% yield. An aq. suspension of (I) and Cu powder shaken with O_2 yields hexahydro-benzaldehyde (chief product) and -benzoic acid. The reaction is not affected by ultra-violet light. R. T.

Mechanism of the Hofmann reaction. Retention of optical activity during the reaction with (+)hydratropamide. C. L. ARBUS and J. KENYON (J.C.S., 1939, 916—920).—The Hofmann rearrangement is substantially an intramol. reaction. Hydratropaldehyde is oxidised by KMnO_4 - MgSO_4 in aq. COMe_2 to *dl*-hydratropic acid, converted, through the strychnine salts, into the (+)-, m.p. 29°, [α]_D²⁰ +74.8° in CHCl_3 , and (−)-acid, m.p. 29°, [α]_D¹⁷ −61.68° (l, 0.5). The (+)-acid, through the chloride and NH_3 at −18°, gives (+)hydratropamide, m.p. 103—104°, which with Br in aq. NaOH affords (−)- α -phenylethylamine, α _D¹⁵ −18.20°, α _D¹⁶ −21.81° (l, 0.5) (Ac derivative, new m.p. 103—104°). Optical activity is almost completely retained during rearrangement. Theoretical aspects are discussed. A. T. P.

Cathodic reduction of aromatic nitroso-compounds.—See A., 1939, I, 378.

Substituted sulphanilamides. I. N^4 -Acyl derivatives. E. MILLER, H. J. ROCK, and M. L. MOORE (J. Amer. Chem. Soc., 1939, 61, 1198—1200).—The following are prepared by the usual methods. N^4 indicates substitution of the *p*- NH_2 of (I). Sulphanilamide* (I), m.p. 165°. N^4 -Acetyl-, m.p. 215—216°, -*propionyl*-, m.p. 220—221°, -*n*-butyryl-, m.p. 230—231°, -*n*-valeryl-, m.p. 197—198°, -*n*-hexoyl-, m.p. 200—201°, -heptyl-, m.p. 192—203°, -octoyl-,

m.p. 200°, -*n*-lauroyl-†, m.p. 205—205.5°, -benzoyl-†, m.p. 280°, -benzyl-, m.p. 169—174°, -isobutyryl-, m.p. 241.5—242.5°, -isovaleryl-, m.p. 216—217°, and -isohexoyl-†, m.p. 193—194°, -sulphanilamide; 4-benzamidobenzenesulphonanilide†, m.p. 222—222.5°; and benzamide-3-sulphonamide†, m.p. 171—173°. Succinic and maleic anhydride and (I) in hot EtOH give *N*-*p*-sulphamidophenyl-succinamic, m.p. 212.5—213.5°, and -maleinamic acid, m.p. 208—209°, respectively; in C_5H_5N 4-succinimidobenzenesulphonamide, m.p. 282.3°, is formed. Substances marked * have high, those marked † no, and others intermediate therapeutic val. against β -haemolytic streptococci in mice. R. S. C.

***p*-Carbamidobenzenesulphonamide.**—See B., 1939, 665.

Alleged optical activity of *o*-toluidine-3:5-disulphonic acid. P. P. HOPF and R. J. W. LE FÈVRE (J.C.S., 1939, 921).—The experiment of Sementzov (A., 1934, 763) with *o*-toluidine-3:5-disulphonic acid is repeated, and gives only inactive acid. The strychnine salt, prepared from excess of acid in $CHCl_3$, has m.p. 245° (decomp.), $[\alpha]_D^{25} +21.0^\circ$ in $CHCl_3$. A. T. P.

Catalytic phenylation of α -naphthylamine and α -naphthylamine-8- and -5-sulphonic acids.—See B., 1939, 576.

Thionitrites. IV. History of nitrosylmercaptides or thionitrites. H. RHEINBOLDT and F. TAPPERMANN [with H. KLEU] (J. pr. Chem., 1939, [ii], 153, 65—76; cf. A., 1932, 599).—Re-examination shows that the compound isolated by Beckurts *et al.* (A., 1906, i, 650) by the addition of HCl or H_2SO_4 to $SH \cdot CH_2 \cdot CO \cdot NHPh$ (I) and KNO_2 in aq. EtOH is nitrosothiolacetanilide, $NO \cdot S \cdot CH_2 \cdot CO \cdot NHPh$, m.p. $\sim 160^\circ$ after becoming colourless at $\sim 100^\circ$, also obtained from (I) and $EtO \cdot NO$. $CH_2Cl \cdot CO_2H$, NH_4CNS , and $NHPhMe$ in EtOH afford carbamylthiolacetmethyl-anilide (II), new m.p. 142—143°, which when heated at $\sim 150^\circ$, followed by extraction of the product with EtOH and treatment of the extract with $Hg(CN)_2$ in boiling MeOH, gives the *Hg* salt, m.p. 118—118.5°, of thiolacetmethyl-anilide, also obtained from (II) by heating with 25% NH_3 in boiling EtOH, acidifying, and adding $Hg(CN)_2$. The mercaptan is oxidised by $FeCl_3$ to dithiodiacetdimethyl-anilide, $(S \cdot CH_2 \cdot CO \cdot NPhMe)_2$, m.p. 81°. Attempts to prepare nitrosothiolacetmethyl-anilide were unsuccessful. Carbamylthiolacet- α -naphthylamide, m.p. 163—164.5°, thiolacet- α -naphthylamide, m.p. 127—128.5° (*Hg* derivative, decomp. $>200^\circ$), and dithiodiacetdi- α -naphthylamide, m.p. 205—206°, are described; nitrosothiolacet- α -naphthylamide could not be obtained pure. Carbamylthioacet- β -naphthylamide, m.p. 180—181° (decomp.), thiolacet- β -naphthylamide (III), m.p. 113—113.5° (*Hg* derivative decomp. 195—210°), and dithiodiacetdi- β -naphthylamide, m.p. 195—198° after partial decomp. at 187°, have been prepared. Nitrosothiolacet- β -naphthylamide, m.p. 194—198° after becoming colourless at 110—115° and brown at 155°, is obtained from (III) and $EtO \cdot NO$. H. W.

Derivatives of diphenyl-*p*-phenylenediamine. J. S. JOFFE and V. J. SOLOVETSHCHIK (J. Gen. Chem. Russ., 1939, 9, 144—148).—4:1:3:6-

T (A., II.)

$NO_2 \cdot C_6H_4Cl_2 \cdot SO_3Na$, $p-NH_2 \cdot C_6H_4 \cdot NHPh$, and Na_2CO_3 in aq. EtOH (10 hr. at the b.p.) yield 5-chloro-2-nitro-4'-anilindiphenylamine-4-sulphonic acid (I) (*K* salt, $+H_2O$). This is reduced (Zn in aq. Na_2CO_3) to the corresponding 2- NH_2 -compound, hydrolysed by boiling 26% HCl to 5-chloro-2-amino-4'-anilindiphenylamine, m.p. 148°. (I) and NH_2Ph in 1:1 H_2O -EtOH (20 hr. at 160—170°/20 atm.) yield 2-nitro-4':5-dianilindiphenylamine-4-sulphonic acid, reduced as before to the 2- NH_2 -compound (attempts at desulphonation unsuccessful). R. T.

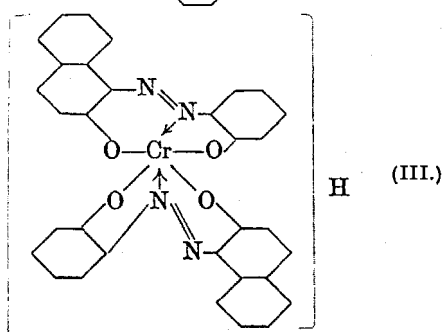
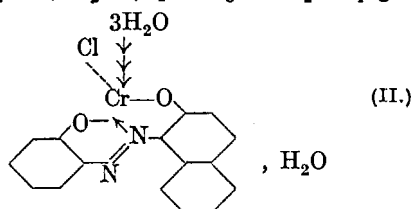
Detection of meta-orientation in diamino-, dinitro-, and aminonitro-compounds. A. ALBERT (J.C.S., 1939, 920—921; cf. A., 1938, II, 458).—*m*-Diamines are detected by the fluorescence (bright yellowish-green) of the diaminoacridines formed by reaction with $ZnCl_2$, glycerol, and $H_2C_2O_4 \cdot 2H_2O$ at 160° for 10 min. A phenolic group interferes with the test. Replacement of half of the $ZnCl_2$ with $SnCl_2$ in the above test allows detection of *m*-orientation in aminonitro- or dinitro-compounds, again giving fluorescing diaminoacridines. Many examples are recorded. A. T. P.

Action of pyridine and ammonia on complex amines of benzidine.—See A., 1939, I, 383.

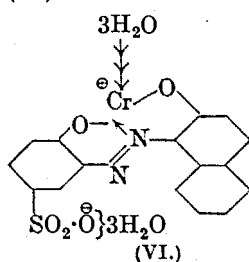
Action of phenylacetic acid on azo-compounds. G. B. CRIPPA and R. CARACCI (Gazetta, 1939, 69, 129—136).—1-Benzeneazo- β -naphthylamine (I) and $CH_2Ph \cdot CO_2H$ (II) at 190° give a substance, m.p. 243—245° (III), and phenylacet- β -naphthylamide (IV), m.p. 159° (identified by synthesis; the α -naphthylamide has m.p. 169°). With $CH_2Ph \cdot CO_2Et$ and a trace of conc. HCl at 220°, (I) gives (III) and (IV). 4-Benzeneazo- α -naphthylamine (V) and (II) give a substance, m.p. 192—195°, and an indulinic (?) substance, m.p. 215°. The indulinic bases obtained from (V) and NH_2Ph at 160—180° give when heated with (II) a product, m.p. 215°, with different properties from the above. E. W. W.

Structure of the chromium lakes of dyes. I. Lakes of *oo'*-dihydroxy- and *o*-hydroxy-*o'*-carboxy-azo-compounds, including monosulphonic acids. Behaviour of azosulphonic acids with chromic salts. H. D. K. DREW and R. E. FAIRBAIRN (J.C.S., 1939, 823—835; cf. A., 1938, II, 180).—A single *o*-OH is insufficient to hold a Cr in stable union with an azo-N; *e.g.*, benzeneazo- β -naphthol and derivatives do not yield complexes with Cr, Fe^{+++} , Mn^{++} , or Zn^{++} (Cu, Co, and Ni give complexes). *o*-Hydroxybenzeneazo- β -naphthol (I) and $CrCl_3 \cdot 4H_2O$ in boiling EtOH (97% unless otherwise stated) afford the H_2O -sol. chromi-chloride tetrahydrate [probably (II)] [$also +2C_5H_5N$ and (impure) $+2NH_2Ph$] (contains ionic Cl and $3H_2O$ co-ordinated with Cr), a complex, $(C_{16}H_{10}O_2N_2)_3Cr_2 \cdot 8H_2O$ (formula given), and an acid chromi-complex (III) (C_5H_5N salt is sol. in H_2O), insol. in H_2O . (III) is also obtained by refluxing (I) and $AcOH \cdot CrCl_3 \cdot 4H_2O$; excess of the latter gives the chromi-acetate salt of (III), also obtained from (II) and $AcOH$. (II) and aq. $H_2C_2O_4$ give some (I). (II) and aq. NH_3 or K_2CrO_4 give the chromi-oxide tetrahydrate (or chromi-hydroxide dihydrate), $(C_{16}H_{10}O_2N_2Cr)_2O \cdot 4H_2O$ (C_5H_5N and NH_2Ph partly

replace co-ordinated H_2O). 2 : 2'-Dihydroxyazobenzene and CrCl_3 give a *chromi-chloride*, $\text{C}_{12}\text{H}_8\text{O}_2\text{N}_2\text{ClCr}, 4\text{H}_2\text{O}$ (aq. NH_3 or K_2CrO_4 gives an



oxide dihydrate, $\text{C}_{24}\text{H}_{10}\text{O}_6\text{N}_4\text{Cr}_2, 2\text{H}_2\text{O}$, insol. in H_2O). 5'-Nitro-2'-hydroxybenzeneazo- β -naphthol (IV) affords a *chromi-chloride*, $\text{C}_{16}\text{H}_9\text{O}_4\text{N}_3\text{ClCr}, 6\text{H}_2\text{O}$ (also $+5\text{H}_2\text{O}$) [*oxide* (?) *octahydrate*, insol. in H_2O], which at $140-160^\circ$ loses all the H_2O and some HCl . 2'-Hydroxy-5'-sulphobenzeneazo- β -naphthol (V) and CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$ in boiling H_2O , or in smaller yield with $\text{K}_2\text{Cr}_2\text{O}_7$ and aq. H_2SO_4 , afford the *chromi-sulphonate*, $+6\text{H}_2\text{O}$ (VI), (NH_4 salt is sol. in H_2O even after desiccation; complex $\text{C}_5\text{H}_5\text{N}$ salt), and a *tribasic acid chromi-complex*, $\text{C}_{32}\text{H}_{21}\text{O}_{10}\text{N}_4\text{S}_2\text{Cr}, 9\text{H}_2\text{O}$ (VII) (2 azo-residues to 1 Cr), also obtained from the Na salt of (V) and (VI) in dil. NaOH . (VI) is sol. in H_2O , and loses $6\text{H}_2\text{O}$ at $140-150^\circ$ and slowly regains $0.5\text{H}_2\text{O}$, but is then insol. in H_2O . (V) and excess of $\text{Cr}_2(\text{SO}_4)_3$ and H_2O give (VII) and a *chromi-sulphonate tetrahydrate*, probably polymerised [boiling aq. NH_3 gives NH_4 salt of (VI)], which loses $3.5\text{H}_2\text{O}$ at $140-170^\circ$ and regains $4\text{H}_2\text{O}$ in 1 month. (VI) and (IV) in aq. NaOH give a *complex*, $\text{C}_{32}\text{H}_{20}\text{O}_9\text{N}_5\text{SCr}, 9\text{H}_2\text{O}$ (VIII) [similar to (VII)], and a *chromi-azosulphonic acid salt* of (VIII), $\text{C}_{48}\text{H}_{29}\text{O}_{14}\text{N}_7\text{S}_2\text{Cr}_2, 14\text{H}_2\text{O}$. Formation of (VI) does not involve oxidation since (VI) and aq.



$\text{H}_2\text{C}_2\text{O}_4$ afford (V). 4'-Hydroxy-*m*-tolueneazo- β -naphthol-6-sulphonic acid (with a little Na sulphonate), refluxed with $\text{Cr}_2(\text{SO}_4)_3$ in H_2O , or $\text{CrCl}_3, 4\text{H}_2\text{O}$ in EtOH , gives a *chromi-sulphonate nonahydrate*, $\text{C}_{17}\text{H}_{11}\text{O}_5\text{N}_2\text{SCr}, 9\text{H}_2\text{O}$ (loses $8\text{H}_2\text{O}$ at $140-150^\circ$; regains $4.5\text{H}_2\text{O}$ and remains sol. in H_2O), and a substance (Cr, 3.6%). 2'-Hydroxy-4'-sulphonaphthalene-1':4-azo-1-phenyl-3-methylpyrazol-5-one and $\text{CrCl}_3, 4\text{H}_2\text{O}$ in EtOH give a *chromi-sulphonate*, $\text{C}_{20}\text{H}_{13}\text{O}_5\text{N}_4\text{SCr}, 5.5\text{H}_2\text{O}$ (loses $4.5\text{H}_2\text{O}$ at $140-170^\circ$; regains $3\text{H}_2\text{O}$ in 10 days, sparingly sol. in H_2O). *o*-Carboxybenzeneazo- β -naphthol (IX) similarly affords

a *chromi-chloride*, $\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2\text{ClCr}, 2.5\text{H}_2\text{O}$ (ionised Cl), converted by boiling H_2O (or aq. NH_3 or K_2CrO_4) into the *oxide tetrahydrate*, $\text{C}_{34}\text{H}_{20}\text{O}_4\text{N}_4\text{Cr}_2, 4\text{H}_2\text{O}$. Naphthalene-1'-azosalicylic acid and $\text{CrCl}_3, 4\text{H}_2\text{O}$ in H_2O (refluxed for 4 hr.) give a *complex*, $\text{C}_{51}\text{H}_{30}\text{O}_9\text{N}_6\text{Cr}_2, 7\text{H}_2\text{O}$ (Cr^{+++} salt of a tribasic chromi-acid) (loses $5\text{H}_2\text{O}$ at 120° ; regains $2.5\text{H}_2\text{O}$), and an (acid) *complex*, $\text{C}_{34}\text{H}_{20}\text{O}_6\text{N}_4\text{Cr}_2, 4.5\text{H}_2\text{O}$ (loses $4\text{H}_2\text{O}$ at 140° ; regains $1\text{H}_2\text{O}$), with properties differing from those of other complexes described. (IX) and $\text{FeCl}_3, 2\text{H}_2\text{O}-\text{EtOH}$ (boil 5 min.) give a *complex*, $[(\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2)_2\text{Fe}]\text{H}, 2\text{H}_2\text{O}$, from which 1 mol. of (IX) is removed by alkali. *p*-Carboxybenzeneazo- β -naphthol (X) and FeCl_3 in $\text{C}_5\text{H}_5\text{N}-\text{EtOH}$ (1:3) give a basic Fe^{III} salt, $(\text{C}_{17}\text{H}_{11}\text{O}_3\text{N}_2)_2\text{Fe}(\text{OH})_2$. (IX) and $\text{Ni}(\text{OAc})_2-\text{EtOH}$ give a *complex*, $\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2\text{Ni}, 2\text{H}_2\text{O}$ (Ni probably ionised from CO_2H) ($2\text{C}_5\text{H}_5\text{N}$ compound), but $\text{Zn}(\text{OAc})_2$ gives a simple salt. (I) in EtOH gives a *ferri-chloride*, $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{ClFe}$, insol. in H_2O , converted by $\text{C}_5\text{H}_5\text{N}-\text{H}_2\text{O}$ into the *complex*, $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{Fe}-\text{OH}, \text{C}_5\text{H}_5\text{N}$. The Ni and Zn complexes of (I) resemble the analogous Cu derivatives; they are co-ordinatively unsaturated, and form $\text{C}_5\text{H}_5\text{N}$ compounds. (V) and aq. FeCl_3 give a *ferri-sulphonate*, $\text{C}_{16}\text{H}_9\text{O}_5\text{N}_2\text{SFe}, 3\text{H}_2\text{O}$, insol. in H_2O , readily decomp. by dil. mineral acids. (X) and chrome alum give Cr^{+++} *p*-carboxybenzeneazo- β -naphthol, $+3\text{H}_2\text{O}$. The Na salt of (X) and aq. CuCl_2 give the simple Cu salt. (X) and $\text{CuSO}_4-\text{aq. NH}_3$ give a *complex*, $\{(\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2)_2\text{Cu}\}\text{Cu}, \text{NH}_3, 6\text{H}_2\text{O}$ (loses $6\text{H}_2\text{O}$ on desiccation; regains $5\text{H}_2\text{O}$ in <2 hr. to give a *pentahydrate*). (X) and $\text{Cu}(\text{OAc})_2$ in $\text{EtOH}-\text{C}_5\text{H}_5\text{N}$ afford the *complex*, $\{(\text{C}_{17}\text{H}_{10}\text{O}_3\text{N}_2)_2\text{Cu}\}\text{Cu}, 2\text{C}_5\text{H}_5\text{N}$, also prepared from the pentahydrate and $\text{C}_5\text{H}_5\text{N}$. Benzene-azosalicylic acid (XI) and $\text{Cu}(\text{OAc})_2-\text{EtOH}$ give a *complex*, $\text{C}_{13}\text{H}_8\text{O}_3\text{N}_2\text{Cu}, 2\text{H}_2\text{O}$, but aq. $\text{CuSO}_4-\text{NH}_3$ affords a *complex* containing 2NH_3 . (XI) and $\text{Ni}(\text{OAc})_2$ in EtOH give a simple Ni salt and a mixture of complexes. Benzeneazo-*o*-cresotic acid and $\text{Cu}(\text{OAc})_2-\text{EtOH}$ yield a *complex*, $\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2\text{Cu}, 2\text{H}_2\text{O}$, whilst cuprammonium sulphate gives a *diammino*-compound, whence the compound, $\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2\text{Cu}, 2\text{C}_5\text{H}_5\text{N}$.

A. T. P.

Decomposition reactions of aromatic diazo-compounds. VI. Reactions of benzenediazonium chloride with metals. W. A. WATERS (J.C.S., 1939, 864-870; cf. A., 1938, II, 52, 405).— PhN_2Cl (I), COMe_2 , and CaCO_3 , with Ag, Au, Cd, Al, In, Mn, Co, Ni, Pd (no PhCl) or Bi (no PhCl), give the metal chloride, $\text{CH}_2\text{Cl}\cdot\text{COMe}$, C_6H_6 , Ph_2 , PhCl , and no organo-metallic compound. Cu and Fe yield also 60 and 20% of PhCl , respectively (catalytic effect). Mg gives MgCl_2 , C_6H_6 , and (?) PhCl , $\text{COMe}_2\cdot\text{CHAc}$, and phorone. Zn (brisk at 0°) affords $\text{ZnCl}_2 + \text{C}_6\text{H}_6$. As gives AsCl_3 , AsCl_5 , and $\text{CH}_2\text{Cl}\cdot\text{COMe}$. B, Ce, Ti, C, Si, ferrosilicon, red P, Ti, Ge, Zr, Th, Cr, W, V, Ta, and Pb do not react; secondary products are sometimes formed. Mo affords also (?) MoCl_5 . (I) does not react with As in the cold, but on heating gives AsPh_2Cl_2 , (?) $\text{AsPh}_3\text{Cl}\cdot\text{OH}$, and *triphenylarsine phenoxhydroxide*, m.p. 129° , converted by $\text{H}_2\text{S}-\text{MeOH}$ into AsPh_3S and PhOH . (I) and Sn in the cold give SnPh_2Cl_2 ; no Pb aryls are obtained (cf. Nesmejanov *et al.*, A., 1936, 66). Theoretical aspects of the reactions are discussed. (I) and CaCO_3 in $\text{COMe}_2-\text{C}_6\text{H}_6$, refluxed for 1 hr., or with Zn dust at room temp.,

give Ph_2 . PhN_2Cl , ZnCl_2 (II) and CaCO_3 in COMe_2 - C_6H_6 -Zn dust give Ph_2 . (I) or (II), C_{10}H_8 , COMe_2 , and Zn give 1- and 2- $\text{C}_{10}\text{H}_7\text{Ph}$ (III). β - C_{10}H_7 - N_2Cl , ZnCl_2 , and Zn in COMe_2 - C_6H_6 give (III). Thus a means is afforded of preparing unsymmetrically substituted diaryls.

A. T. P.

Homologous series of *N*-acyl-*m*-aminophenols and azo-dyes obtained therefrom. H. E. FIERZ-DAVID and H. MEISTER (Helv. Chim. Acta, 1939, 22, 579—585).—*m*-Form-, m.p. 116°, -acet-, m.p. 148°, -propion-, m.p. 181°, -butyr-, m.p. 140°, -valer-, m.p. 119°, -isovaler-, m.p. 143.5°, -hex-, m.p. 135.5°, -hept-, m.p. 147°, -oct-, m.p. 125°, -non-, m.p. 126°, -dec-, m.p. 124.5°, -undec-, m.p. 122.5°, -laur-, m.p. 125°, -tridec-, m.p. 117.5°, -myrist-, m.p. 116°, -pentadec-, m.p. 115.5°, -palmit-, m.p. 114.5°, -margar-, m.p. 114.5°, -stear-, m.p. 114°, -nonadec-, m.p. 115.5°, -ole-, m.p. 95.5°, and -benz-, m.p. 173°, -amidophenol are described. Four series of azo-dyes are obtained by using sulphanilic, metanilic, 6-amino-3-sulphobenzoic acid and 1 : 2 : 5- NH_2 - $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_2$ as azo components. The surface tensions of aq. solutions of these dyes determined by the "abs. tensiometer" of du Nouy give very similar graphs for each homologous series. The min. of the surface tension of 1 in 1000 solutions lies in all cases at a chain-length of 10 or 11 C. The acyl derivatives show a min. here.

H. W.

Derivatives of *o*- and *p*-cyclohexylphenols. D. BODROUX and R. THOMASSIN (Compt. rend., 1939, 208, 1314—1316).—Equimol. amounts of the K derivatives (I) of *o*- or *p*-cyclohexylphenol (cf. A., 1929, 1050) with $(\text{CH}_2\text{Cl})_2$ or $(\text{CH}_2\text{Br})_2$ in boiling EtOH afford the corresponding β -chloro- or β -bromo-ethyl ethers. The following are prepared: *o*- β -chloro-, b.p. 172—174°/10 mm., and β -bromo-ethoxyphenyl-cyclohexane (II), b.p. 183—185°/10 mm.; *p*- β -chloro-, m.p. 56°, and β -bromo-ethoxyphenylcyclohexane (III), m.p. 64°. (II) and (III) (the Cl-compounds give low yields) with hot EtOH-KI afford, nearly quantitatively, *o*-, b.p. 189—191°/10 mm., and *p*- β -iodoethoxyphenylcyclohexane, m.p. 76°, respectively. (I) (2 mols.) with $(\text{CH}_2\text{Br})_2$ (1 mol.) in hot EtOH affords (23%) $\alpha\beta$ -di-*o*-, m.p. 90°, and $\alpha\beta$ -di-*p*-cyclohexylphenoxyethane, m.p. 151°, which with hot dil. EtOH-KOH/6 hr. are decomposed (30—40%) to the original phenols. (II) and (III) with Na in boiling Et₂O afford (80—86%) $\alpha\delta$ -di-*o*-, m.p. 165°, and $\alpha\delta$ -di-*p*-cyclohexylphenoxybutane, m.p. 130°, respectively. (I) with CH_2PhCl or *p*-cyclohexylbenzyl chloride in boiling EtOH affords (>80%) *o*-, b.p. 208—209°/10 mm., and *p*-cyclohexylphenyl benzyl, m.p. 86°, or the *p*-cyclohexylbenzyl ethers, b.p. 282—285°/13 mm., and m.p. 177.5°, respectively, which are stable to hot dil. KOH.

J. L. D.

Condensation of aldehydes and ketones with aromatic compounds in presence of aluminium chloride. I. Condensation of aliphatic ketones with phenols. I. P. TZUKERVANIK and Z. N. NAZAROVA (J. Gen. Chem. Russ., 1939, 9, 33—35).— COMe_2 , COEt_2 , and COMePr^a with PhOH in presence of AlCl_3 at 100° yield respectively *p*-isopropyl-, *p*- α -ethylpropyl-, and *p*- α -methylbutyl-phenol, b.p. 245—250°/730 mm. (benzoate, b.p. 340—350°/730 mm.; acetate, b.p. 254—255°; Me ether, b.p. 232—238°).

R. T.

Derivatives of *p*-tert.-octylphenol.—See B., 1939, 581.

Reactions of Δ^7 -hexene. II. Condensations with aromatic hydrocarbons and phenols. L. SPIEGLER and J. M. TINKER (J. Amer. Chem. Soc., 1939, 61, 1002—1004; cf. A., 1939, II, 238).—Condensation of 1, 2, or 3 mols. of $(\text{CHEt})_2$ with aromatic hydrocarbons or phenols is effected by H_2SO_4 , HClO_4 , or AlCl_3 under the usual conditions, by anhyd. HF at 5—10°, $\text{H}_3\text{BO}_3\text{F}_2$ at the b.p., or ZnCl_2 at 130—180°. The expected products are obtained, but are oils and thus are probably partly isomerised. The following approx. pure compounds are described. *p*-Di- α -ethyl-*n*-butylbenzene, b.p. 104—106°/0.3 mm. *p*-Chloro- α -ethyl-*n*-butylbenzene, b.p. 135—140°/30 mm. *p*- α -Ethyl-*n*-butyltoluene, b.p. 162—165°/135 mm. γ -m-Xylol-, b.p. 101—102°/3 mm., γ -naphthyl-, b.p. 148—151°/1 mm., γ -acenaphthyl-, b.p. 170—174°/4 mm., and γ -chloroacenaphthyl-hexane, b.p. 206—220°/2 mm. Chlorodi- α -ethyl-*n*-butylacenaphthene, b.p. 223—241°/2 mm. Di- α -ethyl-*n*-butylanthracene, b.p. 240—256°/3 mm. α -Ethyl-, b.p. 110°/3 mm., di- α -ethyl-, b.p. 159—175°/2 mm., and tri- α -ethyl-*n*-butylphenol, b.p. 170—195°/7 mm. 6-Chloro- α -ethyl-*n*-butyl-*o*-, b.p. 145—153°/5 mm., and -*m*-cresol, b.p. 155—160°/5 mm. α -Ethyl-*n*-butyl-, b.p. 124—130°/6 mm., and di- α -ethyl-*n*-butyl-cresylic acid, b.p. 165—195°/12 mm. α -Ethyl-*n*-butyl-resorcinol, b.p. 134°/1 mm., -pyrocatechol, b.p. 142—144°/1 mm., -quinol, b.p. 142—151°/2 mm., - α -, b.p. 160—168°/2 mm., and - β -naphthol, b.p. 180—218°/3 mm. Di- α -ethyl-*n*-butylquinol, b.p. 182—190°/3 mm. γ -Phenylhexane, Cl_2 , and I or FeCl_3 give Cl_3 -, b.p. 164—168°/15 mm., Cl_4 -, b.p. 157—162°/5 mm., and Cl_5 -derivatives, b.p. 195—197°/15 mm.

R. S. C.

Hydrofluoric acid as condensing agent. II. Nuclear alkylations in presence of hydrofluoric acid. W. S. CALCOTT, J. M. TINKER, and V. WEINMAYR (J. Amer. Chem. Soc., 1939, 61, 1010—1015; cf. A., 1939, II, 254).—Technical anhyd. or, sometimes, 46% aq. HF causes condensation, usually at 5—10° or 20°, of (a) isocyclic hydrocarbons, phenols or their ethers, nitrophenols or their ethers, carboxylic or sulphonic acids, primary, *sec.*, or *tert.* aminophenols or their ethers with (b) olefines or compounds expected to react as such (e.g., alcohols, ethers, esters, or halides). $\text{C}_{\leq 3}$ -components react more readily than do C_2 -compounds. Migration or isomerisation does not occur. Ethers are unaffected under the reaction conditions and are thus not intermediates; *N*-alkyl derivatives are also not intermediates. $(\text{CH}_2\text{Ph})_2\text{O}$ reacts normally, but $\text{CH}_2\text{Ph-OH}$ polymerises to 1 : 2 : 3 : 4 : 5 : 6-hexaphenylcyclohexane. Diisobutylene gives only Bu⁺ compounds. The dialkylated aminophenols are very unstable, losing NH_3 at room temp., and giving tetra-alkyldiphenylamines when heated. Similarly, only one Pr⁺ could be introduced into quinol, further reaction giving 2 : 4 : 6-triisopropylphenol, b.p. 125°/7 mm. The following are described. α -Chlorotert.-butyl-, b.p. 111°/90 mm., and di- α -chloro-tert.-butyl-benzene, b.p. 140°/4 mm. $\alpha\beta$ -Diphenylpropane, b.p. 109°/2 mm. $\text{C}_{10}\text{H}_7\text{Pr}^a$, m.p. 128° (Cl_4 -derivative, b.p. 170°/0.1 mm.). Naphthylstearic acid, an oil, from C_{10}H and oleic

acid. *iso*Propyltetrahydronaphthalenes, b.p. 136—270°/4.6 mm. *Diisopropyl*-, b.p. 202—206°/0.2 mm., *di-x-ethylbutyl*-, b.p. 240—256°/3 mm., and *penta-x-ethylbutyl-anthracene*, m.p. 89.2—101°. 1-Nitro-*x-iso*propyl-, b.p. 145—155°/2 mm., and *diisopropyl-naphthalene*, b.p. 155—168°/2 mm. (NH_2 -compound, b.p. 150—158°/0.5 mm.). 2-Nitro-4-*isopropylanisole*, b.p. 138.5—139.5°/3 mm. 2-Nitro-4-cyclohexyltoluene, b.p. 198—208°/2 mm. Mixed *iso*propyl-m-, b.p. 102.5°/4 mm., m.p. 43°, *benzyl-o*-, b.p. 160°/5 mm., and *dibenzyl-o-cresol*, b.p. 235°/5 mm. *iso*Propylquinol, m.p. 147—148°. Di- α -ethyl-*n-butyl*diphenyl ether, b.p. 200—230°/5 mm. *Diisopropyl- β -naphthol*, b.p. 196°/2 mm. 2-Hydroxy-*x-iso*propyl-, m.p. ~50, and -*polyisopropyl-3-naphthoic acid*, m.p. 70—75°. *Polyisopropyl-naphthalene-2-sulphonic acid*, m.p. ~40°. *m-iso*Propylbenzoic acid, m.p. ~20° (chloride, b.p. 125—130°/23 mm.). 4-Amino-*xx-diisopropylphenol*, b.p. 120°/2 mm. (sulphate, m.p. 206—208°). 4:4'-*Dihydroxytetraisopropyl-diphenylamine*, b.p. 228°/4 mm. 4-Dimethylamino-*x-isopropylphenol*, m.p. 99—104°, b.p. 137°/3 mm., and *diisopropylphenol*, b.p. 148°/3 mm. *Diisopropyl-p-anisidine*, b.p. 128°/3.6 mm. 4:4'-*Dimethoxytetraisopropyl-diphenylamine*, b.p. 230—234°/3 mm. (hydrochloride). *cyclo*Hexyl-*p-anisidine tetrahydrofluoride*, m.p. 185—195°, and *hydrochloride*, m.p. 225—230°. 3-Ethoxy-*x-isopropyl-NN-diethylaniline*, b.p. 110°/0.15 mm. 2-Methoxy-*xxx-triisopropyl- α -naphthylamine*, b.p. 169°/0.14 mm. R. S. C.

Preparation of 3:6-di- and 3:4:6-tri-bromopyrocatechol. J. FREJKA and B. ŠEFRÁNEK (Coll. Czech. Chem. Comm., 1939, 11, 165—170; cf. A., 1936, 602).—*iso*Propylidenepyrocatechol (prep. by COMe_2 and P_2O_5 at 60°) gives the 3:6- Br_2 -derivative, m.p. 92°, hydrolysed by conc. H_2SO_4 at 60° to 3:6-dibromopyrocatechol, m.p. 122° (Ac_2 derivative, m.p. 109°), which with Br-CHCl_3 affords the 3:4:6- Br_3 -derivative, m.p. 135—136° (Ac_2 derivative, m.p. 115°), and was previously (Sloof, A., 1936, 838) considered to be the 4:5- Br_2 -compound. R. S. C.

Synthetic oestrogenic compounds related to stilbene and diphenylethane. I. E. C. DODDS, L. GOLBERG, W. LAWSON, and (SR) R. ROBINSON (Proc. Roy. Soc., 1939, B, 127, 140—166; cf. Kerschbaum *et al.*, A., 1939, II, 259).—A more detailed account of work previously reviewed (A., 1938, III, 299, 807, 908). δ -Phenyl- γ -anisylhexan- γ -ol, b.p. 140—143°/0.3 mm. (from *p*- $\text{OMe-C}_6\text{H}_4\text{-CO-CHPhEt}$ and MgEtBr), is dehydrated ($\text{PBr}_3\text{-CHCl}_3$) to *p-methoxy- $\alpha\beta$ -diethylstilbene*, b.p. 140—144°/0.25 mm., demethylated by EtOH-KOH at 190°/20 hr. to *p-hydroxy- $\alpha\beta$ -diethylstilbene*, b.p. 135—140°/0.15 mm. Anisil and MgEtBr give $\gamma\delta$ -dianisylhexane- $\gamma\delta$ -diol, m.p. 193—194° [also obtained with m.p. 192—195° from *p*- $\text{OMe-C}_6\text{H}_4\text{-COEt}$ and Mg-Hg at 100° (bath)/7 days; reduced (red P, conc. HI) to a compound, $\text{C}_{18}\text{H}_{22}\text{O}_2\text{, H}_2\text{O}$, m.p. 64.5—65°], together with α -anisyl- α -anisylpropyl alcohol, m.p. 105—107°, and (probably) $\alpha\beta$ -dianisylbutane- $\alpha\beta$ -diol, b.p. 215—220°/0.25 mm. α -Ethyldeoxyanisoin, b.p. 192—195°/0.65 mm. (from deoxyanisoin and EtI in EtOH-NaOEt), and MgEtBr give $\gamma\delta$ -dianisylhexan- γ -ol, m.p. 115—117°, b.p. 194—196°/0.8 mm. (*p*-nitrobenzoate, m.p. 120—122°),

dehydrated ($\text{PBr}_3\text{-CHCl}_3$ at 0°-room temp.; KHSO_4 at 195—200°; boiling $\text{Ac}_2\text{O-AcCl}$) to 4:4'-dimethoxy- $\alpha\beta$ -diethylstilbene, forms, m.p. 123—124° (I) and b.p. 175—178°/0.74 mm. (*cis*) (II) [gradually converted into (I) by sunlight]. Demethylation of (I) by AlCl_3 or AlBr_3 was not successful but EtOH-KOH at 200—210°/24 hr. yields (trans)-4:4'-dihydroxy- $\alpha\beta$ -diethylstilbene [diethylstilbæstrol] (III), m.p. 171° (diacetate, m.p. 123—124°; dipropionate, m.p. 104°; di-n-, m.p. 88°, and -*iso*-butyrate, m.p. 86—87°; di-n-valerate, m.p. 89°; dipalmitate, m.p. 77—78°; dibenzoate, m.p. 210—211°; di- α -, m.p. 206—207°, and - β -naphthoate, m.p. 252—253°; bisphenylacetate, m.p. 100°); (II) similarly affords (III) and its *cis*-isomeride [ψ -diethylstilbæstrol] (IV), m.p. 140—142° (diacetate, m.p. 116—117°; dibenzoate, m.p. 193—197°). Reduction [AcOH-HI (*d* 1.94)] of (I) gives a product, $\text{C}_{18}\text{H}_{22}\text{O}_2$, b.p. 189—190°/0.8 mm., which is undoubtedly a mixture. Reduction (H_2 , PtO_2 , EtOH) of (IV) affords an alkali-insol. saturated substance, b.p. 184—187°/21 mm. and a saturated compound, $\text{C}_{18}\text{H}_{22}\text{O}_2$, m.p. 181—182°. Reduction (H_2 , Pd-C , COMe_2) of (III) yields a $\gamma\delta$ -di-*p*-hydroxyphenylhexane (V), m.p. 128° (Me_2 ether, m.p. 56—57°), whilst (IV) similarly gives a $\gamma\delta$ -*p*-hydroxyphenylhexane (VI), m.p. 185°, together with some (III) (isomeric change) and hence (V); (I) and (II) both yield the Me_2 ether, m.p. 145—146°, of (VI). Similar reduction of (IX) (below) also gives (VI). The dibenzoate, m.p. 138—140°, of 4:4'-dihydroxy- α -ethyldeoxybenzoin (VII), b.p. 210—215°/0.6 mm. (acetate, m.p. 91—92°) (from α -ethyldeoxyanisoin and AcOH-HI), with MgEtBr affords a product which heated to 150°/~0.3 mm. yields (III). The dibenzyl ether, m.p. 78—80°, of (VII) and MgEtBr give $\gamma\delta$ -di-*p*-benzyloxyphenylhexan- γ -ol, forms, m.p. 142—144° and 212—214°, converted by $\text{PBr}_3\text{-CHCl}_3$ into crude (III). $\alpha\beta$ -Dianisylbutan- β -ol, b.p. 178—181°/0.6 mm., m.p. 61—62° (from deoxyanisoin and MgEtBr), is dehydrated [as for (I)] to 4:4'-dimethoxy- α -ethylstilbene, b.p. 165—166°/0.75 mm., m.p. 85°, demethylated (EtOH-KOH) to 4:4'-dihydroxy- α -ethylstilbene, b.p. 208—211°/0.3 mm., m.p. 128—129° (dibenzoate, m.p. 100—102°). $\beta\beta$ -Dianisylbutan- β -ol, m.p. 87—89° [from α -methyldeoxyanisoin (VIII), b.p. 176—177°/0.1 mm., m.p. 53—57°, and MgMeI], similarly gives 4:4'-dimethoxy-, m.p. 127—129°, and thence 4:4'-dihydroxy- $\alpha\beta$ -dimethylstilbene [dimethylstilbæstrol], m.p. 194—196° (accompanied by some of its Me_2 ether, m.p. 115—116°). 4:4'-Dimethoxy- α -methyl- β -ethylstilbene, b.p. 159—161°/0.14 mm. [from (VIII) and MgEtI], is demethylated (EtOH-KOH at 200—210°) to the 4:4'-(OH) $_2$ -derivative [methyl-ethylstilbæstrol], m.p. 179—180° (dibenzoate, m.p. 217—219°). α -*n*-Propyldeoxyanisoin, b.p. 195—196°/0.14 mm., and MgEtBr give $\gamma\delta$ -dianisylheptan- γ -ol, b.p. 176—177°/0.3 mm., whence 4:4'-dimethoxy-, b.p. 192—195°/0.4 mm. (also obtained directly from ethyldeoxyanisoin and excess of MgPr^nBr), and 4:4'-dihydroxy- α -ethyl- β -*n*-propylstilbene, b.p. 198—200°/0.14 mm. (dibenzoate, m.p. 208—211°). 4:4'-Dimethoxy- and 4:4'-dihydroxy- $\alpha\beta$ -di-*n*-propylstilbene have b.p. 178—181°/0.8 mm. and 198—201°/0.69 mm., respectively. α -*iso*Propyldeoxyanisoin, b.p. 210—214°/0.8 mm., with MgPr^nBr affords $\gamma\delta$ -dianisyl- $\beta\epsilon$ -dimethylhexan- γ -ol, b.p. 205—207°/0.27 mm., dehydr-

ated (KHSO₄) to 4:4'-dimethoxy-, b.p. 181—182°/0.25 mm. (accompanied by a little 4:4'-dimethoxystilbene, m.p. 214°), whence 4:4'-dihydroxy- α - β -diisopropylstilbene, b.p. 202—204°/0.25 mm. (dibenzoate, m.p. 155°). 4:4'-Dimethoxy-, b.p. 186—188°/0.16 mm. (from α -n-butyldeoxyanisoin, b.p. 205—206°/0.6 mm., and MgBu⁺Br), and 4:4'-dihydroxy- α - β -di-n-butylstilbene, b.p. 191—196°/0.2 mm. (dibenzoate, m.p. 192—193°), are prepared. Ethyldeoxyanisoin, Mg, and a little MeI in Et₂O followed by CH₂:CH·CH₂Br (dropwise in Et₂O) give 4:4'-dimethoxy- α -ethyl- β -allylstilbene, b.p. 197—198°/0.8 mm., which is demethylated and probably isomerised by EtOH-KOH to 4:4'-dihydroxy- α -ethyl- β -propenylstilbene, b.p. 208—211°/0.17 mm. (dibenzoate, m.p. 111—113°). α -Allyldeoxyanisoin, b.p. 196—198°/0.13 mm., Mg, I, and MeI (little) in Et₂O followed by CH₂:CH·CH₂Br afford $\delta\epsilon$ -dianisyl- $\Delta^{\alpha\gamma}$ -octadien- ϵ -ol, b.p. 198—203°/0.23 mm., dehydrated (KHSO₄) to 4:4'-dimethoxy- α - β -diallylstilbene, b.p. 186—188°/0.09 mm., converted by EtOH-KOH into 4:4'-dihydroxy- α - β -dipropenylstilbene, b.p. 220—226°/0.4 mm. (dibenzoate, m.p. 164°). Me dianisyladipate-a (A., 1933, 828) and MgMeI give $\delta\epsilon$ -dianisyl- $\beta\gamma$ -dimethyloctane- $\beta\gamma$ -diol-a, m.p. 125—126°, dehydrated (KHSO₄) to $\delta\epsilon$ -dianisyl- $\beta\gamma$ -dimethyl- $\Delta^{\beta\epsilon}$ -octadiene, b.p. 202—203°/0.14 mm., which is reduced (H₂, PtO₂, EtOH) to the -octane, b.p. 210—220°/0.3 mm., and demethylated to $\delta\epsilon$ -di-p-hydroxyphenyl- $\beta\gamma$ -dimethyl- $\Delta^{\beta\epsilon}$ -octadiene, b.p. 215—220°/0.01 mm. (dibenzoate, m.p. 71—72°). α -Phenyl- α - β -dianisylethyl alcohol, m.p. 111—112° (from deoxyanisoin and MgPhBr), is dehydrated (Ac₂O-AcCl) to 4:4'-dimethoxy- α -phenylstilbene, forms, m.p. 105—106° and 92—93°, whence (EtOH-KOH at 200°) the 4:4'-(OH)₂-derivative, m.p. 99—100°. $\gamma\delta$ -Di-p-hydroxyphenylhexane- $\gamma\delta$ -diol, m.p. 204—206° (diacetate, m.p. 199—200°) (from p-OH·C₆H₄·COEt and Al-Hg in moist Et₂O), with boiling Ac₂O-AcCl gives the diacetate, m.p. 119—120°, of $\gamma\delta$ -di-p-hydroxyphenyl- $\Delta^{\beta\epsilon}$ -hexadiene (IX), m.p. 227—228° (dipropionate, m.p. 96°). $\delta\epsilon$ -Di-p-hydroxyphenyloctane- $\delta\epsilon$ -diol, m.p. 186—187° (diacetate, m.p. 198—199°) (from p-OH·C₆H₄·COPr), similarly affords the diacetate, m.p. 129—130°, of $\delta\epsilon$ -di-p-hydroxyphenyl- $\Delta^{\alpha\gamma}$ -octadiene, m.p. 127—128°. $\beta\gamma$ -Di-p-hydroxyphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 164—165° (diacetate, m.p. 118—119°), is similarly obtained from (p-OH·C₆H₄·CMe₂·OH)₂. $\alpha\delta$ -Diphenyl- $\beta\gamma$ -di-p-hydroxyphenylbutane- $\beta\gamma$ -diol, m.p. 197—198° (diacetate, m.p. 208—209°) (from p-OH·C₆H₄·CO·CH₂Ph and Al-Hg in moist Et₂O), similarly yields $\alpha\delta$ -diphenyl- $\beta\gamma$ -di-p-hydroxyphenyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 231—232° (diacetate, m.p. 202°). α -Phenyl- $\beta\gamma$ -di-p-hydroxyphenylethylene, m.p. 178°, is obtained from the (OMe)₂-derivative and EtOH-KOH at 190°/18 hr.

m-OMe·C₆H₄·COMe (modified prep.; cf. A., 1937, II, 356) and p-OMe·C₆H₄·CHO in aq. EtOH-NaOH at 0° give m-anisyl p-methoxystyryl ketone [4:3'-dimethoxychalkone], m.p. 52°, which with NaCN in boiling MeOH (aq. AcOH being added so that the reaction mixture remains slightly alkaline) affords γ -keto- α -cyano- α -p-anisyl- γ -m-anisylpropane, m.p. 96—97°, hydrolysed (AcOH-conc. H₂SO₄) to β -m-anisoyl- α -p-anisylpropionamide, m.p. 136—137°, and thence (aq. EtOH-NaOH) to the acid, m.p. 161—162°, which is reduced (Clemmensen) to γ -m-anisyl- α -p-

anisylbutyric acid, m.p. 98—99°. This with boiling POCl₃ yields 1-keto-6-methoxy-2-anisyl-1:2:3:4-tetrahydronaphthalene, m.p. 126—127°, converted by MgEtBr into 6-methoxy-2-anisyl-1-ethyl-3:4-dihydronaphthalene, m.p. 94—95°, which is demethylated and reduced by EtOH-KOH at 165°/36 hr. to 6-hydroxy-2-p-hydroxyphenyl-1-ethyl-1:2:3:4-tetrahydronaphthalene, m.p. 256° (sinters at 225°) (dibenzoate, m.p. 213—215°). 5:14-Dihydroxy-1:2:9:10:11:18-hexahydrochrysene-a, m.p. 263—264°, is obtained from the (OMe)₂-derivative (A., 1933, 828) and AcOH-HI (d 1.9). II. B.

Synthesis of derivatives of s-diphenylethane related to materials occurring naturally. II. 3'-Methoxy-5-methyl-3:4-dihydrodibenzyl, a compound related to cestrone in structure. S. NATELSON and S. P. GOTTFRIED (J. Amer. Chem. Soc., 1939, 61, 1001—1002; cf. A., 1936, 1248).—Conversion of m-C₆H₄Br·NO₂ into the amine and thence (diazo-reaction) into m-C₆H₄Br·OH (>80% yield) and its Me ether, b.p. 105/16 mm., is described. m-OMe·C₆H₄·MgBr with (CH₂)₂O gives β -m-anisylethyl alcohol, b.p. 148°/13 mm., converted by SOCl₂ into the chloride, b.p. 122°/18 mm.; the Grignard reagent thereof condenses with 3-methyl- Δ^2 -cyclohexenone (prep. from CH₃Ac·CO₂Et, 40% aq. CH₂O, and a little piperidine in EtOH), yielding 3'-methoxy-5-methyl-3:4-dihydrodibenzyl, b.p. 184°/10 mm., which is rapidly polymerised by 80% H₂SO₄. R. S. C.

Catalytic hydrogenation of vanillin. Vanillyl-creosol. A. S. PFAU (Helv. Chim. Acta, 1939, 22, 550—554).—Hydrogenation (Pd-C in AcOH) at atm. pressure and room temp. of vanillin yields creosol and 4:5'-dihydroxy-3:4'-dimethoxy-2'-methyl-diphenyl-methane, m.p. 108.5—109°. The Me₂ ether, m.p. 75—76°, is oxidised by CrO₃ in warm AcOH or by SeO₂ at 200—210° to 3:4:4':5'-tetramethoxy-2'-methyl-benzophenone (I), m.p. 124—124.5°, converted by NaNH₂ in boiling C₆H₆ into veratric acid, veratrole (II), and homoveratrole. The synthesis of (I) from 6-methylveratric acid and (II) is described. H. W.

Oxidation of derivatives of vanillin with peracetic acid. J. BOESEKEN and J. GREUP (Rec. trav. chim., 1939, 58, 528—537; cf. A., 1936, 1510).—3:4-Dimethoxy-, 3-methoxy-4-ethoxy-, 4-methoxy-3-ethoxy-, 3:4-diethoxy-, 3-methoxy-4-butoxy-, 3-ethoxy-4-butoxy-, or 4-benzoyloxy-3-methoxy- (poor yield of phenol) benzaldehyde, with AcO₂H (prep. described) + 0.5% p-C₆H₄Me·SO₃H in AcOH, give the corresponding dialkoxypheols (as acetates). 3:4-Dimethoxy-, new m.p. 81.5°, 3-methoxy-4-ethoxy-, new m.p. 46—48°, 4-methoxy-3-ethoxy-, new m.p. 77—78°, and 3:4-diethoxy-phenol, m.p. 65.5—66.5°, and 3-methoxy-, m.p. 24—25°, and 3-ethoxy-4-butoxyphenol, m.p. 58°, are described. Acetyl- or 2:4-dinitrophenyl-vanillin, however, similarly afford respectively acetylvanillic acid or a mixture (or 1:1 compound), m.p. 212—215°, of vanillic acid and its 2:4-dinitrophenyl ether. A. T. P.

Reactions of aminophenols with copper and iron. V. A. NAZARENKO (J. Appl. Chem. Russ., 1939, 12, 151—154).—p-Aminophenol and its derivatives give intense colorations with Cu^{II} or Fe^{III}

salts. The reactions are made more sensitive by addition of halides, in the order $\text{Cl}' > \text{Br}' > \text{CNS}' > \text{I}'$, and consist initially in oxidation of aminophenol, followed by formation of coloured complexes of the oxidation products with Fe or Cu. The most sensitive reagent for detection of Cu is 2:4-diaminophenol in presence of KBr (1 p.p.m. of Cu). R. T.

Aminohydroxydiarylmethanes.—See B., 1939, 580.

Migration of ester groups in the hydroxylated phenyl- β -naphthylamine series. W. DILTHEY and H. PASSING (J. pr. Chem., 1939, [ii], 153, 26—34).—1-Anilino- β -naphthol (I), m.p. 158—159° (lit. 153—154°, 155—156°), with BzCl and K_2CO_3 in hot COMe_2 gives the N-Bz derivative (II), m.p. 202—203° [hydrolysed to (I) by Na-Hg], but with BzCl and KOH in aq. COMe_2 gives the O-benzoate (III), m.p. 161—162°, resolidifying with m.p. 202—203°. When heated at 205—210° or warmed with alcoholic alkali, (III) is converted into (II). With BzCl in hot $\text{C}_5\text{H}_5\text{N}$ (I) gives the ON-Bz₂ derivative, m.p. 166—167°, hydrolysed by alkali to (II). β - $\text{C}_{10}\text{H}_7\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot p$ (IV) and BzCl in hot $\text{C}_5\text{H}_5\text{N}$ give the ON-Bz₂ derivative, m.p. 145—146°, hydrolysed by KOH-MeOH to the N-Bz derivative, m.p. 182—183°. With BzCl and K_2CO_3 in hot COMe_2 or with $\text{BzCl-KOH-H}_2\text{O-N}_2$, (IV) gives the O-benzoate, m.p. 165—166°, hydrolysed to (IV) by KOH-MeOH . Acetylation of (IV) gives only the N-Ac derivative, m.p. 231—232°. R. S. C.

Syntheses in the phenanthrene series. X. 8-Methoxy-1-methylphenanthrene. J. LOCKETT and W. F. SHORT (J.C.S., 1939, 787—790; cf. A., 1938, II, 134).—2:6-Dimethylcyclohexanone and $\text{Mg } \beta$ -o-anisylethyl chloride give 1- β -o-anisylethyl-2:6-dimethylcyclohexan-1-ol, b.p. 185°/3.5 mm., dehydrated by KHSO_4 to the Δ^1 -cyclohexene, b.p. 165—168°/7 mm., which with AlCl_3 , then S, affords 8-methoxy-1-methylphenanthrene, m.p. 117.5—118° (picrate, m.p. 151—152°), identical with that obtained by Kon *et al.* (A., 1939, II, 326); the compound, m.p. 96—97°, stated to be this (*loc. cit.*) is wrongly named (cf. A., 1938, II, 273). 5:1-NH₂·C₁₀H₆·OH and Ac_2O (5 mols.) at room temp. give 5-acetamido-1-naphthol, m.p. 176—177°; its Me ether, m.p. 189—190°, and conc. HCl-EtOH give 5-methoxy-1-naphthylamine, m.p. 80—81°. The Grignard solution from 1-iodo-5-methoxynaphthalene (by diazo-reaction), m.p. 79—80°, and $(\text{CH}_3\text{CO})_2\text{O}$ (method: *loc. cit.*) give β -5-methoxy-1-naphthoyl-propionic acid (I). Coumarin, Na, and $\text{C}_6\text{H}_{11}\text{OH}$ or EtOH give γ -o-hydroxyphenylpropyl alcohol, b.p. 176—178°/12 mm., methylated to γ -o-anisylpropyl alcohol (II), b.p. 145—146°/10 mm. (3:5-dinitrobenzoate, m.p. 113—114°). Methylation of coumarin (method: Reimer *et al.*, A., 1928, 288) gives Me O-methylcoumarinate, b.p. 150—163°/10 mm., and o-methoxycinnamic acid; catalytic reduction then gives Me β -o-anisylpropionate (III), b.p. 146—147°/10 mm., and β -o-anisylpropionic acid, m.p. 85.5—86°, respectively. (III) or the corresponding Et ester, with Na-EtOH , gives (II), which with SOCl_2 and NPhMe_2 or $\text{C}_5\text{H}_5\text{N}$ affords the chloride, b.p. 120—

130°/10 mm., and thence ($\text{KCN-EtOH-NaI-CuSO}_4$) the nitrile, b.p. 135—145°/12 mm., hydrolysed by KOH-MeOH to γ -o-anisylbutyric acid, m.p. 39—39.5° (IV), and a little γ -o-anisylpropyl Me ether, b.p. 120—122°/10 mm. (IV) and $\text{P}_2\text{O}_5\text{-C}_6\text{H}_6$, or best with POCl_3 in boiling $\text{C}_2\text{H}_5\text{Cl}$, give 1-keto-5-methoxy-1:2:3:4-tetrahydronaphthalene, m.p. 89—89.5° (semicarbazone, m.p. 249—250°). The Reformatsky reaction, followed by P_2O_5 , then gives Et 5-methoxy-3:4-dihydro-1-naphthylacetate, b.p. 160—175°/0.6 mm., reduced by Na-EtOH to β -5-methoxy-1:2:3:4-tetrahydro-1-naphthylethyl alcohol (V) (3:5-dinitrobenzoate, m.p. 107—108°) and a little 5-methoxy-1:2:3:4-tetrahydronaphthylacetic acid, m.p. 146—147°. (V) and $\text{PBr}_3\text{-NPhMe}_2\text{-CHCl}_3$ at $< 5^\circ$, then room temp., afford the bromide (decomp. on distillation), converted by $\text{CHK(CO}_2\text{Et)}_2$ in PhMe into the malonic ester, hydrolysed to β -5-methoxy-1:2:3:4-tetrahydro-1-naphthylethylmalonic acid, m.p. 124—126°, decarboxylated at 190—210° to γ -5-methoxy-1:2:3:4-tetrahydro-1-naphthylbutyric acid, m.p. 67—68°. The latter and S (2 atoms) at 190—210° give γ -5-methoxy-1-naphthylbutyric acid (VI), m.p. 143°, also obtained by Clemmensen reduction of (I). (VI) is dehydrated ($\text{P}_2\text{O}_5\text{-C}_6\text{H}_6$ or SnCl_4) to 7-keto-4-methoxy-7:8-dihydrohomophenalene, m.p. 88—89° (semicarbazone, new m.p. 227—228°) [previously described (A., 1938, II, 134) as 1-keto-8-methoxy-1:2:3:4-tetrahydrophenanthrene; the latter compound, m.p. 137°, is correctly described by Kon *et al.*, A., 1936, 465], which with MgMeI , then dehydrogenation with S, gives a little of a compound, m.p. 105—106° (picrate, m.p. $\sim 157^\circ$), which is not a methoxymethylphenanthrene. The compound described as 8-methoxy-1-methyl-3:4-dihydrophenanthrene (*loc. cit.*) is 4-methoxy-7-methylhomophenalene.

A. T. P.

Mobility of groups in 3-chloro-4-nitro- and 5-chloro-2-nitro-diphenylsulphones. J. D. LOUDON (J.C.S., 1939, 902—906; cf. A., 1938, II, 477).—The mobility of groups in the sulphones is largely but not completely controlled by the activating influence of the NO_2 -substituent. 1:3:4- $\text{C}_6\text{H}_3\text{Cl(NO}_2)_2$ and PhSH-NaOH-aq.EtOH give Ph_2S_2 , and 4- and 5-chloro-2-nitrodiphenyl sulphide, m.p. 127° [sulphone (I), m.p. 186—187°]; use of high temp. or excess of PhSH , or the latter and (I) in dioxan-EtOH, give 2:4-diphenylthiolnitrobenzene (II), m.p. 120° [$\text{H}_2\text{O}_2\text{-AcOH}$ give the disulphone (III), m.p. 160°]. (I) and piperidine or NaOMe in MeOH-dioxan afford 2-nitro-5-piperidinodiphenylsulphone, m.p. 192°, or (some) 1:5:2- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{ClNO}_2$, respectively. (I) and $\text{NH}_3\text{-MeOH}$ at 160° afford 2:5:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{ClNH}_2$ and 2:4-diphenylsulphonylaniline, m.p. 203°, also obtained from (III) and $\text{NH}_3\text{-EtOH}$ or $\text{SnCl}_2\text{-HCl-AcOH}$. Similarly prepared are: 5-chloro-2-nitro-4'-methylidiphenyl sulphide, m.p. 127° (sulphone, m.p. 189°); 2:4-di-p-tolylthiolnitrobenzene, m.p. 105° (disulphone, m.p. 158°), and 2-nitro-5-piperidino-4'-methylidiphenyl sulphide, m.p. 178°. 3-Aminodiphenylsulphone and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl-C}_5\text{H}_5\text{N}$ give 3-p-toluenesulphonamido-diphenylsulphone, m.p. 152°, nitrated by boiling HNO_3 (d 1.4)-AcOH to 4-nitro-3- (IV), m.p. 220°, 2-nitro-5-, m.p. 152° [2-nitro-5-aminodiphenylsulphone, m.p. 235—236°, is converted (Sandmeyer) into (I)],

and 2:4-dinitro-5-*p*-toluenesulphonamidodiphenylsulphone, m.p. 173° [also by further nitration of (NO₂)₁-compounds; corresponding 5-NH₂-derivative, m.p. 241°]. (IV) is hydrolysed by 80% H₂SO₄ at 110° to 4-nitro-3-aminodiphenylsulphone (V), m.p. 185°, which (or its 3-nitro-4-amino-isomeride) with SnCl₂-HCl-EtOH gives 3:4-diaminodiphenylsulphone, m.p. 126° (whence 6-phenylsulphonyl-2:3-diphenylquinazoline, m.p. 196°). 3-Acetamidodiphenylsulphone, m.p. 143°, and HNO₃ (d 1.5) at 0° give the 4-, m.p. 154°, and 2-NO₂-derivative, m.p. 187°, hydrolysed by H₂SO₄ at 110° to (V) and 2-nitro-3-aminodiphenylsulphone, m.p. 171°, respectively. 3-Chloro-4-nitrodiphenylsulphone (VI), m.p. 133° (by Sandmeyer reaction), and piperidine or NaOMe in MeOH-dioxan give 4-nitro-3-piperidino-, m.p. 116°, and 3-chloro-4-methoxy-diphenylsulphone, m.p. 111° (+ some nitromethoxy-compound), respectively. (VI) and SnCl₂-AcOH-HCl or NH₃-MeOH at 180° give 3-chloro-4-aminodiphenylsulphone, m.p. 197°, with (V) also in the latter reaction. (VI) and PhSH-NaOH-aq. EtOH give 4-nitro-3-phenylthiodiphenylsulphone (VII), m.p. 166–167° [convertible into (II) or (III)]. Piperidine and (III) at 100°, or NaOMe in boiling MeOH-dioxan, afford solely 1-piperidino-2:4-diphenylsulphonylbenzene, m.p. 156°, or 2:4-diphenylsulphonylanisole, m.p. 176°, respectively. (III) and PhSH-NaOH-aq. EtOH give (VII) and 2:4-diphenylsulphonyldiphenyl sulphide, m.p. 221°, oxidised to 1:2:4-triphenylsulphonylbenzene, m.p. 198°. Similarly prepared are: 1-piperidino-2:4-di-*p*-tolylsulphonylbenzene, m.p. 163°; 2:4-di-*p*-tolylsulphonyl-4'-methylidiphenyl sulphide, m.p. 220°; 1:2:4-tri-*p*-tolylsulphonylbenzene (IX), m.p. 185°; and 4-nitro-3-*p*-tolylthiol-4'-methylidiphenylsulphone, m.p. 124°. 1:3:4-C₆H₃Cl(NO₂)₂ and *p*-C₆H₄Me·SO₂Na, refluxed with dioxan-(CH₂·OH)₂, give (IX) and 5-chloro-2-nitro-4'-methylidiphenylsulphone. A. T. P.

Syntheses with *o*- and *p*-hydroxydiphenyls.
III. 2-Hydroxydiphenyl-5-sulphonic acid and its derivatives. N. N. VOROSHCYV, jun., and A. T. TROSCHTSCHENKO (J. Gen. Chem. Russ., 1939, 9, 59–64).—*o*-C₆H₄Ph·OH and H₂SO₄ at room temp. or at 100° yield 2-hydroxydiphenyl-5-sulphonic acid (I) (Ca salt, +4H₂O). This heated for 5 hr. at 150° with Ac₂O, and the product treated with PCl₅ (4 hr. at 100°), yields 2-acetoxydiphenyl-5-sulphonyl chloride, m.p. 76–77°, which affords 2-hydroxy-, m.p. 146–147°, or 2-acetoxy-diphenyl-5-sulphonanilide (II), m.p. 141–142°, respectively with excess and the theoretical amount of NH₂Ph. (II) and Ac₂O (100 min. at 100°) yield 2-acetoxydiphenyl-5-sulphonacetanilide, m.p. 138–139°. (I) and HNO₃-H₂SO₄ give 3-nitro-2-hydroxydiphenyl-5-sulphonic acid (III) (Na, K, and Ca salts), converted by hot dil. HNO₃ into 3:5-dinitro-2-hydroxydiphenyl, and by HCl into 3-nitro-2-hydroxydiphenyl. 5-Bromo-, m.p. 113–115°, and 5-chloro-3-nitro-2-hydroxydiphenyl, m.p. 129–131°, are obtained by the action of Br and Cl₂ on (III) (at room temp.), or by nitration and halogenation of *o*-C₆H₄Ph·OH. (III) is reduced (Sn in HCl) to 3-amino-2-hydroxydiphenyl-5-sulphonic acid, from which a red-violet azo-dye is obtained by diazotisation and coupling with α-C₁₀H₇·OH. R. T.

Internal and external field action of substituents on methyl donors and acceptors.—See A., 1939, I, 376.

Reaction of styrene oxide with magnesium methyl iodide. C. GOLUMBIC and D. L. COTTLE (J. Amer. Chem. Soc., 1939, 61, 996–1000).—MgMeI reacts with styrene oxide (I) and CHPhI·CH₂·OH at room temp., but with CH₂I·CHPh·OH only when heated; CH₂Ph·CHMe·OH (phenylcarbamate, new m.p. 86.5–87°) is produced in all cases, and the alcohols sometimes give some CH₂Ph·CH₂·OH. With MgMe₂, (I) gives CHPhMe·CH₂·OH, and α-epoxypropane gives *sec*-BuOH. HI converts (I) in Et₂O or H₂O into CHPhI·CH₂·OH. HgO-I converts CHPhI·CH₂ in wet Et₂O into CH₂I·CHPh·OH, m.p. 34°. R. S. C.

Chloroalkylation of *p*-propylanisole. Synthesis of some derivatives. R. QUELET and J. DECASSE (Compt. rend., 1939, 208, 1317–1319; cf. A., 1934, 290).—Saturation of *p*-C₆H₄Pr·OMe, CH₂O, and ZnCl₂ with dry HCl at 40° affords 2-methoxy-5-propylbenzyl chloride (75%) (I), b.p. 140–145°/17 mm. (some decomp.), and a little 2:2'-dimethoxy-5:5'-dipropylidiphenylmethane, m.p. 51° (I) with (CH₂)₆N₄ gives 2-methoxy-5-propylbenzaldehyde (II), b.p. 151°/16 mm. (semicarbazone, m.p. 239°), oxidised (KMnO₄) to 4-methoxysulphthalic acid, m.p. 275°. (I) with NaOAc affords (after hydrolysis) 2-methoxy-5-propylbenzyl alcohol, b.p. 163°/16 mm. (Me, b.p. 141°/16 mm., and Et ether, b.p. 147°/17 mm.; phenylcarbamate, m.p. 53°), which when heated with a trace of HCl gives di-(2-methoxy-5-propylbenzyl) ether, b.p. 240–245°/16 mm., m.p. 62°, decomposed by heat into (II) and 2:4:1-C₆H₃MePr·OMe (cf. A., 1936, 1504). *p*-C₆H₄Pr·OMe with (MeCHO)₃, dil. H₃PO₄, and dry HCl (A., 1936, 719) affords 2-α-chloroethyl-4-propylanisole (undistillable), which with C₆H₅N at 115° gives 2-methoxy-5-propylstyrene, b.p. 124–125°/16 mm., converted by O₃ into (II). J. L. D.

Action of mixed nitric and sulphuric acids on 5-bromo-3:6-dinitro-1:2:4-trimethylbenzene. I. J. RINKES (Rec. trav. chim., 1939, 58, 538–543; cf. A., 1939, II, 111, 159).—The "nitrate," new m.p. 152–153°, of Huender (*loc. cit.*) is a mixture of 4-bromo-3:6-dinitro-2:5- (I), m.p. 155.5–156°, and 5-bromo-3:6-dinitro-2:4-dimethylbenzyl nitrate (II), m.p. 154°. 2:5:4:1-C₆H₂Me₂Br·CH₂Cl (III) and (CH₂)₆N₄ in 60% EtOH give 2:5:4:1-C₆H₂Me₂Br·CHO, m.p. 60–61° [semicarbazone, m.p. 243° (decomp.)]; (III) and Pb(NO₃)₂ give 4-bromo-2:5-dimethylbenzyl alcohol, m.p. 96°. (III), HNO₃ (d 1.5), and 10% oleum at 65° afford 4-bromo-3:6-dinitro-2:5-dimethylbenzyl chloride, m.p. 139°; the iodide, m.p. 166°, and AgNO₃ in dioxan give (I). 2:4:5:1-C₆H₂Me₂Br·CH₂Cl similarly gives 5-bromo-3:6-dinitro-2:4-dimethylbenzyl iodide, m.p. 153° (via the chloride, m.p. 128°), and thence (II) (cf. Smith *et al.*, A., 1937, II, 338). A. T. P.

Synthesis of growth-inhibitory polycyclic compounds. I. G. M. BADGER and J. W. COOK (J.C.S., 1939, 802–806).—Attempts are made to prepare compounds which can be used to control growth of tumours. *o*-1-Naphthoylebenzoic acid and BzCl-

H_2SO_4 at 130° for 1 hr. give 1:2-benzanthraquinone, reduced by $\text{SnCl}_2\text{--HCl--AcOH}$ to the anthranol and thence by Zn--NaOH to 1:2-benzanthracene. The latter and dry HCl , $(\text{CH}_2\text{O})_x$, and AcOH at 60° , or $(\text{CH}_2\text{Cl})_2\text{O--AcOH}$ at 80° , afford 10-chloromethyl-1:2-benzanthracene (I), m.p. 186.5—187°, and (by former method) some 10:10'-di-(1:2-benzanthran-yl)methane, m.p. $>300^\circ$; (I) is hydrogenated (Pd-black--COMe_2) to 10-methyl-1:2-benzanthracene. (I) and KOAc--AcOH afford, through the acetate of (II), m.p. 148.5—149.5° (cf. Fieser *et al.*, A., 1938, II, 406) (hydrolysed by NaOH--EtOH), 10-hydroxymethyl-1:2-benzanthracene (II), m.p. 170—172° [$(\text{CH}_2\text{CO})_2\text{O--C}_5\text{H}_5\text{N}$ at 100° gives the *H succinate*, m.p. 185.5—186°]. (I) and KCN--EtOH give 10-ethoxymethyl-1:2-benzanthracene, m.p. 90—90.5°; no nitrile is formed. (I) and $\text{C}_5\text{H}_5\text{N}$ at room temp. afford the pyridinium chloride, m.p. 205—208° (decomp.) (corresponding picrate, m.p. 199—201°), and (I) and piperidine at 100° (bath) give *N*-(1:2-benzanthran-yl-10-methyl)-piperidine hydrochloride, m.p. 251—253° (decomp.) (free base, m.p. 106—107°). (I) and $\text{CHNa}(\text{CO}_2\text{Et})_2\text{--C}_6\text{H}_6$ at room temp. overnight, then boiling for 6 hr., give *Et* (1:2-benzanthran-yl-10-methyl)malonate, m.p. 120—120.5°, and a by-product, m.p. 224—225°. The corresponding malonic acid, m.p. $\sim 200^\circ$ (*Na* salt), is decarboxylated at 210—220° to β -(1:2-benz-10-anthran-yl)propionic acid, m.p. 210—211°. Chloromethyl derivatives are not obtained from 9- or 10-methyl-1:2-benzanthracene, 3:4-benzpyrene, or 20-methylcholanthrene. Anthracene, dry HCl , and $(\text{CH}_2\text{O})_x$ in AcOH at 60° give 9:10-di(chloromethyl)anthracene (III), decomp. 204—205°. 9:10-Dimethoxy-9:10-dimethyl-9:10-dihydroanthracene and Na in $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ give 9:10-dimethylan- thracene, which with $\text{Pb}(\text{OAc})_4\text{--AcOH}$ at 100° (bath) for 15 min. affords 9:10-di(acetoxymethyl)anthracene, m.p. 224—225°, also obtained from (III) and KOAc--AcOH . Thus high reactivity of Me groups is not sp. for the carcinogenic hydrocarbon. 9:10-Dimethyl-1:2-benzanthracene (IV) and Br--CS_2 at -10° give 9:10-di(bromomethyl)benzanthracene, m.p. 208—209°, converted by KOAc--AcOH into the di(acetoxymethyl) derivative, m.p. 167—168°, also obtained from (IV) and $\text{Pb}(\text{OAc})_4\text{--AcOH}$. Hydrolysis (KOH--EtOH) yields 9:10-di(hydroxymethyl)-1:2-benzanthracene, m.p. 222—223° (H_2 disuccinate, m.p. 199.5—200.5°). A. T. P.

Reactions in sunlight. E. OLIVERI-MANDALÀ, A. GIACALONE, and E. DELEO (Gazzetta, 1939, 69, 104—110; cf. A., 1938, II, 361).—Acenaphthene and Bz_2 in sunlight give, in addition to the product $\text{C}_{26}\text{H}_{20}\text{O}_2$ (I), m.p. 234° (*loc. cit.*), the 2:1 mol. compound, m.p. 137° , of Bz_2 and benzoin. With Ac_2O , (I) gives a Ac_2 derivative, m.p. 195—196°, and a substance, m.p. 187—188°; (I) is therefore regarded as 1:2-dihydroxy-1:2-diphenyl-3:4-1':8'-naphthylene-cyclobutane. Acenaphthene, with or without CH_2Ph_2 , and acenaphthenequinone with $\text{C}_2\text{H}_5\text{Ph}_2$ are unaltered in sunlight. CHPh_3 and COPh_2 in C_6H_6 give CPh_3OH . E. W. W.

Reduction of $\alpha\beta$ -diketones. R. B. THOMPSON (J. Amer. Chem. Soc., 1939, 61, 1281—1283).—1:4-Reduction is shown to be the first step for $\alpha\beta$ -

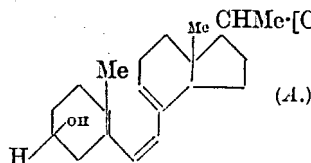
diketones. Dimesityl diketone (I) absorbs only 1 H_2 when hydrogenated (PtO_2) in abs. MeOH , and forms an unusually stable enediol, $\alpha\beta$ -dihydroxy- $\alpha\beta$ -dimesitylethylene, m.p. 149—151°; this product is isolated in 70% yield by working in N_2 , but in air re-forms (I). It decolorises 2:6-dichloroindophenol, gives a dibenzoate (II), m.p. 235° [with KOH--EtOH gives (I) by hydrolysis and oxidation], and is fairly stable in MeOH containing piperidine, slowly giving the benzoin. Addition of (I) to MgEtBr and then of BzCl give (cf. Fuson *et al.*, A., 1939, II, 260) a dibenzoate, m.p. 188—189°, which is stereoisomeric with (II). Hydrogenation (PtO_2) of diketones normally shows no signs of 1:4-addition, but hydrogenation (H_2 , PtO_2 , little HCl , and ZnCl_2) in Ac_2O gives a β -diacetate, m.p. 107—108° (lit. 110°). From benzil, and $\text{CHPh}_2\text{CO--COPh}$ gives $\alpha\beta$ -diacetoxymethyl- α -phenyl- β -benzhydrylethylene, m.p. 132.5—133.5°, hydrolysed to $\text{CHPh}_2\text{CO--CHPh--OH}$ (acetate, m.p. 67—68°). R. S. C.

Ether-like compounds. V. Preparation of ethers of triphenylcarbinol. E. J. SALMI and E. RENKONEN (Ber., 1939, 72, [B], 1107—1108).—Calc. amounts of CPh_3OH and the requisite OH-compound are subjected to azeotropic distillation in C_6H_6 containing a little $p\text{-C}_6\text{H}_4\text{Me--SO}_3\text{H}$ as catalyst. When reaction is finished the acid is neutralised by solid K_2CO_3 . The method has been applied with cetyl alcohol, $\text{CH}_2\text{Ph--OH}$, $\text{OH}\cdot[\text{CH}_2]_2\text{OMe}$, $\text{OH}\cdot[\text{CH}_2]_2\text{O--CH}_2\text{Ph}$, $\text{OH}\cdot\text{CH}_2\text{CO}_2\text{Pr}^i$, *l*-menthol, and technical borneol. Triphenylmethyl β -benzyloxyethyl ether, m.p. 73—74°, and Pr^i triphenylmethoxyacetate, m.p. 99.5—100.5°, are new. H. W.

Sensitive test for ergosterol and differentiation of ergosterol and ergosteryl esters. A. F. VON CHRISTIAN and V. ANGER (Ber., 1939, 72, [B], 1124—1125).—The sample is dissolved in a few drops of CHCl_3 and the solution is treated with 90% $\text{CCl}_3\text{CO}_2\text{H}$ (1 c.c.) and one drop of 0.5% $\text{Pb}(\text{OAc})_4$ solution; in the presence of ergosterol (I) a rose-violet colour is developed. Treatment of a solution of the sterol in CHCl_3 with 5% $\text{Pb}(\text{OAc})_4$ followed by $\text{CCl}_3\text{CO}_2\text{H}$ gives a green fluorescence if (I) is present, and a violet-rose colour in presence of ergosteryl esters. A microchemical form of the test is described. H. W.

Products of irradiation of 22-dihydroergosterol. A. WINDAUS and B. GÜNTZEL (Annalen, 1939, 538, 120—127).—In general, the photochemical transformation of 22-dihydroergosterol (I) resembles that of ergosterol and 7-dehydrocholesterol. Exposure of (I) in C_6H_6 to light of long λ leads to lumisterol₄ (II) ($+x\text{H}_2\text{O}$), m.p. 101° , $[\alpha]_D^{20} +187^\circ$ in COMe_2 (3:5-dinitrobenzoate, m.p. 141° , $[\alpha]_D^{20} +11.5^\circ$ in CHCl_3), which does not give an additive product with vitamin- D_4 . It is assumed to be formed in the same manner as lumisterol by steric transformation at C_{10} , and hence may be named 22-dihydrolumisterol. Exposure of (I) in peroxide-free Et_2O to Mg light yields tachysterol₄ (III), the acetate of which gives with citraconic anhydride (IV) an additive compound, m.p. 156° , $[\alpha]_D^{20} +79.5^\circ$ in CHCl_3 ; the identity of this compound with that obtained by Lettré (A., 1934, 887) by hydrogenation of the

tachysterol acetate-(IV) adduct proves (III) to be a 22-dihydrotachysterol (A). During the prep. of



(II) and (III), vitamin- D_4 (Windaus *et al.*, A., 1937, III, 327) is obtained; for it and its 3:5-dinitrobenzoate the consts., m.p. 96–98°, $[\alpha]_D^{25} +85.7^\circ$ in COMe_2 , and m.p. 127–128°, $[\alpha]_D^{25} +93.2^\circ$ in COMe_2 , are now recorded. Very protracted exposure of (I) to Mg light leads to *suprasterol*, m.p. 132°, $[\alpha]_D^{25} +261^\circ$ in COMe_2 (3:5-dinitrobenzoate, m.p. 161°, $[\alpha]_D^{25} +214^\circ$ in CHCl_3), the ultra-violet absorption spectrum of which does not indicate the presence of conjugated double linkings. H. W.

Steroids. XX. New colour reaction in the steroid series and its chemistry. H. KÄGI and K. MIESCHER (Helv. Chim. Acta, 1939, 22, 683–697).—The substance (1–2 mg.) is dissolved in glacial AcOH (1–2 c.c.) and boiled for a few sec. after addition of 1 drop of conc. H_2SO_4 . After cooling, a 1% solution of Br in AcOH is added dropwise. The solution becomes intensely blue to violet. The colour is discharged by an excess of Br. Ac_2O may replace Br, whereby the colour is not developed so rapidly but is not discharged by an excess of the reagent. Under these mild conditions the change is given by substances with OH in the cisoid position at C_{17} . The following reaction is given also by substances with OH in the transoid position at C_{17} . The compound (1–2 mg.) is boiled for a short time with POCl_3 in quinoline; after cooling, the mixture is dissolved in AcOH (1–2 c.c.) and conc. H_2SO_4 (2–3 drops) is added followed by 1% Br-AcOH. The success of the Liebermann-Burchard reaction for sterols with a C chain at C_{17} , depends on the presence of at least one nuclear double linking or of groups from which such linking can be derived. The chemistry of the reaction is examined at the instance of the androstan-17-ols. Either of these is converted by KHSO_4 or CuSO_4 into ψ -androsterone (I), $[\alpha]_D^{25} -25^\circ$ in EtOH, which gives a marked colour change in $\text{AcOH-H}_2\text{SO}_4$ with Cl_2 , Br, I, Ac_2O , succinic anhydride, Bz_2O_2 , or CrO_3 or in AcOH-HBr or $\text{AcOH-H}_3\text{PO}_4$ with halogens but not with aliphatic anhydrides. It does not appear to be homogeneous. In AcOH containing KOAc it absorbs ~ 4 Br; it is hydrogenated (PtO_2 in AcOH) to ψ -androsterane (II) which does not give a colour with H_2SO_4 -Br but is unsaturated towards $\text{C}(\text{NO}_2)_4$. Its absorption curve differs from that of Δ^{16} -androsterone (III), and indicates the presence of a conjugated double linking. It becomes resinified when preserved, particularly if exposed to light. Dehydrogenation (Se) of (I) or (II) gives a substance identical with or closely analogous to 3-methylcyclopentenophenanthrene. Treatment of (I) in AcOH-HBr with 4 Br gives a brown, resinous powder which gives a blue colour in AcOH. It contains only $\sim 11\%$ of Br and passes when kept into a material which does not colour AcOH. Steroids with *tert.*-

OH at C_{17} , do not appear to yield similar chromogens. Androstane-3 β :17 α -diol 17-hexahydrobenzoate is converted by $p\text{-C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ into the 3- p -toluenesulphonate, which passes in boiling quinoline into Δ^2 -androsten-17 α -ol hexahydrobenzoate, m.p. 117°. This is hydrogenated (PtO_2 in AcOH) to androstan-17 α -ol hexahydrobenzoate, m.p. 138–139°, hydrolysed to androstan-17 α -ol, m.p. 152–153°, which is converted by Tschugaev's method into (III), m.p. 44.5–45°, $[\alpha]_D^{25} +18.5^\circ$ in EtOH, which gives only a slight colour with Br in H_2SO_4 -AcOH. H. W.

Constituents of the adrenal cortex and related substances. XXV. *alloPregnane-3:17*-diol derivatives of the 17(β) series. Further evidence of the adherence of substances P and K to the 17(β) series. T. REICHSTEIN and C. MEYSTRE (Helv. Chim. Acta, 1939, 22, 728–741).—The crude product of the addition of C_2H_2 to *trans*-androsterone is acetylated and the monoacetate of the 17(α) compound is separated as far as possible by crystallisation. The mother-liquors are treated with Girard's reagent T and the unchanged material, after re-acetylation and eventual removal of more (I), is chromatographed (Brockmann's Al_2O_3), thus leading to Δ^{20} -*allopregnine-3-trans-17(β)-diol 3-monoacetate* (II), m.p. 174–175°, $[\alpha]_D^{25} +27^\circ \pm 6^\circ$ in COMe_2 (free diol, m.p. 228–229°). *trans*-Dehydroandrosterone is treated with C_2H_2 and the product is worked up analogously, thereby giving $\Delta^{5:20}$ -*pregnenine-3-trans-17(β)-diol 3-monoacetate* (III), m.p. 186–188°, $[\alpha]_D^{25} -26.3^\circ \pm 2^\circ$ in COMe_2 (free diol, m.p. 243–245°), which gives an immediate ppt. with AgNO_3 in MeOH. (II) and (III) are hydrogenated (PtO_2 in EtOH-AcOH) to *allopregnane-3-trans-17(β)-diol 3-monoacetate*, m.p. 174–178°, $[\alpha]_D^{25} -20.05^\circ \pm 2^\circ$ in COMe_2 (free diol, m.p. 174°, and, after re-solidification, m.p. 187°). Ozonisation of (II) in CCl_4 at -10° and treatment of the ozonide with Zn dust-AcOH followed by hydrolysis of the product gives 3-*trans*-17(β)-dihydroxy Δ^5 -cholonic acid, m.p. 263–268°, identical with that derived from substance P [the identity is further confirmed by comparison of the Me ester (IV) (acetate, m.p. 184–186°, $[\alpha]_D^{25} +7.09^\circ \pm 2^\circ$ in COMe_2) from the two sources]. A neutral by-product of the ozonisation is *trans*-androsterone acetate. (III) treated with Br in CCl_4 , then ozonised, and the product decomposed and debrominated gives 3-*trans*-17(β)-dihydroxy Δ^5 -cholonic acid, m.p. 247–249° (decomp.) [Me ester (V), m.p. 238–240°, $[\alpha]_D^{25} -61.9^\circ \pm 10^\circ$ in COMe_2], and *trans*-dehydroandrosterone acetate. The free diols of the 17(β) series are distinguished from the analogous products of the 17(α) series since they give an immediate, very sparingly sol. ppt. with digitonin in hot solution. This behaviour is shown by (IV) and (V). M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XXIII. Partial synthesis of substance J. M. SUTTER, C. MEYSTRE, and T. REICHSTEIN (Helv. Chim. Acta, 1939, 22, 618–625).—Distillation in a high vac. of *allopregnane-3 β :17 α -diol 3-acetate* with anhyd. CuSO_4 gives a colourless liquid (I) containing 3- β -acetoxy- Δ^{17} -pregnene but mainly isomeric compounds with a different position

of the double linking and transformation products which do not have the *allopregnane* skeleton. Hydroxylation of (I) by OsO_4 followed by alkaline hydrolysis gives a small amount of *allopregnane-3:17:20-triol*, isolated as the diacetate, identical with substance J; the configuration at $\text{C}_{(17)}$ and $\text{C}_{(20)}$ remains uncertain. The main product is another *triol* (II), m.p. 194—195° (corr.), converted by Ac_2O and $\text{C}_5\text{H}_5\text{N}$ at room temp. into an *acetate*, m.p. 182—184° (corr.), $[\alpha]_D^{25} -7.65^\circ \pm 2^\circ$ in COMe_2 , oxidised to a neutral product, $\text{C}_{23}\text{H}_{36}\text{O}_4$, m.p. 102—104°. CrO_3 in AcOH oxidises (II) to a neutral compound, m.p. 148—152° (corr.); the non-formation of androstenedione shows that (II) is not a *allopregnane-3:17:20-triol*. Two further acetates, m.p. 192° and 160° (corr.), respectively, were obtained in very small amount.

H. W.

Derivatives of Δ^5 -androstene-3:17-diol-17-acetic acid and of Δ^5 -pregnene-3:17:21-triol. T. REICHSTEIN, H. MÜLLER, C. MEYSTRE, and M. SUTTER (Helv. Chim. Acta, 1939, 22, 741—753).—*t*-Dehydroandrosteroe acetate is converted by $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Zn filings activated with I in boiling C_6H_6 followed by hydrolysis of the product into Δ^5 -androstene-3:17-diol-17-acetic acid (I), m.p. 246—247° (corr.) [*Me* ester (II), m.p. 151—153° (corr.), or, as hydrate, m.p. 95—98° and 145—149° after re-solidification]. (I) is transformed by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at room temp. into its 3-monoacetate, m.p. 206—209° (corr.), the *Me* ester (III), m.p. 66—68° and 111—113° (corr.) after re-solidification, of which is obtained with CH_2N_2 or directly in the Reformatsky reaction if $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}$ is used. Boiling Ac_2O or the protracted action of Ac_2O in $\text{C}_5\text{H}_5\text{N}$ converts (I) into the 3:17-diacetate, m.p. 210—211° (corr.) (*Me* ester, m.p. 110—112°); the 3-monobenzoate of the *Me* ester has m.p. 180—183°. Boiling SOCl_2 followed by hydrolysis ($\text{KOH}\cdot\text{MeOH}$) converts (III) into Δ^5 -pregnadien-3-ol-21-carboxylic acid, m.p. 217—218°, better obtained by distilling (III) with anhyd. CuSO_4 under 12 mm. (I) or (II) is transformed by MgPhBr into the very hygroscopic Δ^5 -21:21-diphenyl- Δ^5 -pregnene-3:17:21-triol (IV), m.p. variable (~130—132°), $\text{CPh}_2\cdot\text{CH}_2$, and *t*-dehydroandrosteroe. With Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at room temp. or 100° (IV) gives the 3-monoacetate, m.p. 228—232° (corr.), whereas acetylation at 134° appears to give 3-acetoxy-21:21-diphenyl- Δ^5 -20-pregnatriene, m.p. 193—195° (corr.), in poor yield. MgMeBr and (II) afford 21:21-dimethyl- Δ^5 -pregnene-3:17:21-triol, m.p. 268—274° (corr.), converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ at room temp. or at 100° into the 3-monoacetate, m.p. 170—174° (corr.), whereas at 134° the main product is a 3-acetoxy-21:21-dimethylpregnatriene, m.p. 110—118°; at 111° the (impure) triacetate, m.p. 92—96°, appears to result. Reduction ($\text{Na}\cdot\text{EtOH}$) of (II) gives Δ^5 -pregnene-3:17:21-triol, m.p. 243—245° (corr.) [*diacetate*, m.p. 159—160° (corr.), $[\alpha]_D^{25} -65.3^\circ \pm 1.5^\circ$ in COMe_2], and a pregnenetriol, m.p. 180—183° (corr.) (monoacetate, m.p. 160—161°).

H. W.

Alepric and aleprylic acids, new homologues of chaulmoogric acid. H. I. COLE and H. T. CARDOSO (Science, 1939, 89, 200; cf. B., 1938, 811).—Alepric acid (I), m.p. 48°, $[\alpha] +77^\circ$, the next lower homologue

(by C_2H_4) to hydnocarpic acid, and aleprylic acid, m.p. 32°, $[\alpha] +90^\circ$, the next lower homologue (by C_2H_4) to (I), have been isolated by repeated vac. distillation of the Et esters from *Hydnocarpus wightiana* and fractional crystallisation of the free acids.

L. S. T.

Esters of chaulmoogric and hydnocarpic acid and of chaulmoogryl and hydnocarpyl alcohol. III. K. BURSCHKIES (Ber., 1939, 72, [B], 1012—1016; cf. A., 1938, II, 139, 441).—Chaulmoogryl chloride and $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$ in boiling Et_2O and N_2 give β -bromoethyl chaulmoograte, b.p. 190—192°/0.3 mm., converted by $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Ag}$ in xylene at 130° into ethylene glycol β -cinnamate α -chaulmoograte, b.p. 220—240°/0.1 mm. $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ and $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$ in boiling Et_2O afford β -bromoethyl cinnamate, m.p. 47—48°, transformed by Na hydnocarpate in xylene at 130° into ethylene glycol β -cinnamate α -hydnocarpate, b.p. 230—240°/0.1 mm., also obtained (b.p. 230—235°/0.05 mm.) from β -hydroxyethyl hydnocarpate, b.p. 198—200°/0.03 mm. Na oleate and $\text{Br}\cdot[\text{CH}_2]_2\cdot\text{OH}$ in xylene at 140° yield β -hydroxyethyl oleate, b.p. 190—200°/0.05 mm., transformed by hydnocarpyl chloride and $\text{C}_5\text{H}_5\text{N}$ in PhMe at 130° into ethylene glycol β -hydnocarpate α -oleate, b.p. 270—280°/0.15 mm. Hydnocarpyl chaulmoograte, b.p. 240—260°/0.1—0.5 mm., m.p. 33—34°, is described. Hydnocarpyl glycolate, b.p. 180—210°/0.05 mm., m.p. 34.5°, is converted into hydnocarpyl chaulmoogroyloxyacetate, b.p. 260—280°/0.01 mm., m.p. 24—25°, also obtained from hydnocarpyl chloroacetate, b.p. 180—190°/0.1 mm. Chaulmoogryl cinnamoyloxyacetate, b.p. 240—250°/0.05 mm., and hydnocarpyl oleoyloxyacetate, b.p. 260—280°/0.03 mm., have been obtained. Many of the esters are tolerated better than the known chaulmoogric esters.

H. W.

Reductions with phosphorus in presence of iodine or hydrogen iodide as catalyst. K. MIESCHER and J. R. BILLETER (Helv. Chim. Acta, 1939, 22, 601—610).—Reduction can frequently be effected without use of HI and in open vessels provided that sufficient P is present; either I or an iodide may be used with mineral acid as diluent. HCl is adequate for temp. ~100°. H_2SO_4 is useless since it is reduced by HI. For higher temp. H_3PO_4 is recommended, the b.p. of which can be adjusted by suitable addition of H_2O . Although the substances are frequently insol. in the medium, the reduction proceeds smoothly. The amount of I or I' required is usually only a fraction of the calc. quantity, the min. amount being 2—15%. If it is necessary to work with solutions use is made of AcOH or of EtCO_2H or other higher fatty acid if higher temp. are required. The following reductions are described: $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ to $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$; COPhMe to $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPhMe}$; $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ to $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$; $\text{OH}\cdot\text{CPhMe}\cdot\text{CO}_2\text{H}$ to $\text{CHPhMe}\cdot\text{CO}_2\text{H}$; $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ to $\text{CHPh}_2\cdot\text{CO}_2\text{H}$;

$\text{o}\cdot\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ to $\text{C}_6\text{H}_4\cdot\left\langle\begin{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \\ \text{CO} \end{smallmatrix}\right\rangle\text{O}$ with

KI in dil. H_3PO_4 (at 130°) or dil. HCl, with I in AcOH or in H_3PO_4 at 150° if <10% of the calc. amount of catalyst is used, or to $\text{o}\cdot\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ with >10% of catalyst in H_3PO_4 at 150°, in

HCl at 140–145°, or in EtCO₂H at 141°; CH₂Bz·CH₂·CO₂H to Ph·[CH₂]₃·CO₂H and 1-keto-1:2:3:4-tetrahydronaphthalene; *o*-C₆H₄Bz·CO₂H to dihydroanthracene; *p*-C₆H₄Me·SO₂R (R = Cl, NH₂, or NHPh) to *p*-C₆H₄Me·SH; *m*-CO₂H·C₆H₄·SO₂Cl to *m*-SH·C₆H₄·CO₂H; PhOMe to PhOH and MeI (a mol. amount of iodide is requisite). H. W.

Perkin's cinnamic acid synthesis. G. LOCK and E. BAYER (Ber., 1939, 72, [B], 1064–1071).—The decrease in the reactivity of aldehydes in Perkin's synthesis which is caused by Me groups can be counteracted by NO₂-groups. Cl, Br, or I in the *p*-position do not influence the rate of reaction greatly whereas F causes a marked diminution of yield. With Br- and particularly with I-derivatives there is considerable formation of resinous products. Restriction caused by Et or Ph markedly exceeds that due to Me and corresponds nearly with that observed with 2:4:6-C₆H₂Me₃·CHO. OMe groups generally diminish the rate of the synthesis. The presence of substituents has also a very marked effect on the yields obtained in Knoevenagel's synthesis of cinnamic acid but the effects in this and in the Perkin reaction are not parallel. Thus *p*-C₆H₄Et·CH:CH·CO₂H is obtained in very good yield by the former but with difficulty by the latter method. The following are new: 3:5-dinitro-2:4:6-trimethylcinnamic acid, m.p. 294° (corr.; decomp.) [Et ester, m.p. 121° (corr.)], converted by Br in CHCl₃ into αβ-dibromo-β-3:5-dinitro-2:4:6-trimethylphenylpropionic acid, decomp. ~212° after ill-defined melting; *p*-ethylcinnamic acid, m.p. 143° (dibromide, m.p. 130°); 2:6-dibromo-3:4-dimethoxycinnamic acid, m.p. 175.5° (corr.). *p*-C₆H₄Et·CHO could not be obtained satisfactorily from PhEt by the Gattermann-Koch method. *p*-C₆H₄ClAc is reduced (Clemmensen) to *p*-C₆H₄EtCl in 27% yield but this substance did not react satisfactorily with CuCN. PhEt, COCl·CO₂Et, and AlCl₃ in Cl₂ yield *p*-C₆H₄Et·CO·CO₂Et, hydrolysed to C₆H₄Et·CO·CO₂H, whence C₆H₄Et·C(NPh)·CO₂H, C₆H₄Et·CH·NPh, and *p*-C₆H₄Et·CHO in 23% yield. H. W.

Optically active stereoisomeric alicyclic acids, alcohols, and aldehydes. M. MOUSSERON and R. GRANGER (Compt. rend., 1939, 208, 1500–1502).—The keto-form of 2-chloro-5-methylcyclohexanone with NaOMe gives only 2-hydroxy-5-methylcyclohexanone, whereas the enol form gives 60% of Me 3-methylcyclopentanecarboxylate (cf. A., 1938, II, 184), which by fractional distillation gives the *cis*-(?), b.p. 168°/760 mm., [α]₅₇₉ –39.43°, and *trans*-(?), b.p. 169°/760 mm., [α]₅₇₉ –5.96°, isomerides, hydrolysed to *cis*-, b.p. 116°/15 mm., [α]₅₇₉ –41.42°, and *trans*-3-methylcyclopentanecarboxylic acid, b.p. 117.5°/15 mm., [α]₅₇₉ –13.96°. The esters with Na in EtOH give *cis*-, b.p. 85°/24 mm., [α]₅₇₉ –34.71°, and *trans*-, b.p. 86°/24 mm., [α]₅₇₉ –3.37°, -3-methylcyclopentylcarbinol, respectively, also separable by crystallisation of the H phthalates. Oxidation of the active carbinols gives inactive aldehydes. Active *trans*-3-methylcyclohexanol with HCl or PCl₅ affords 3-chloro-1-methylcyclohexanes (A), converted (Grignard) into 60 or 10–15%, respectively, of (probably) *cis*-, b.p. 134°/25 mm., [α]₅₇₉ –1.62° (Me ester, b.p. 191°/

760 mm., [α]₅₇₉ –5.29°), and *trans*-3-methylcyclohexanecarboxylic acid, b.p. 132°/15 mm., [α]₅₇₉ +1.54° (Me ester, b.p. 193°/760 mm., [α]₅₇₉ +2.21°) (cf. A., 1938, II, 400). (A) with CH(OEt)₃ gives *cis*-, b.p. 176°/760 mm., [α]₅₇₉ –8.97° (semicarbazone, m.p. 135°), and *trans*-3-methylcyclohexylformaldehyde, b.p. 178°/760 mm., [α]₅₇₉ +4.16° (semicarbazone, m.p. 157°), separated by crystallising their semicarbazones. They are also formed by the distillation of (active) 1-methyl-3-methylenecyclohexane oxide (cf. Tiffeneau *et al.*, A., 1937, II, 414), but oxidation (CrO₃) of *cis*-, b.p. 95°/25 mm., [α]₅₇₉ –5.45°, and *trans*-, b.p. 96°/25 mm., [α]₅₇₉ –4.43°, -3-methylcyclohexylcarbinols gives inactive products. J. L. D.

Alkaline dehalogenation of 1-chlorocyclohexyl methyl and phenyl ketone. Transformation into 1-substituted cyclohexane-1-carboxylic acids. B. TCHOUBAR and O. SACKUR (Compt. rend., 1939, 208, 1020–1022).—cycloHexyl Me ketone with SO₂Cl₂ affords 1-chlorocyclohexyl Me ketone (I), b.p. 87–89°/15 mm., converted into 1-hydroxycyclohexyl Me ketone (II) (semicarbazone, m.p. 205°), which is dehydrated (H₂C₂O₄) to Δ¹-cyclohexenyl Me ketone (semicarbazone, m.p. 220°). (I) with dry powdered KOH for 2–3 hr. gives K 1-methylcyclohexane-1-carboxylate, identified as the amide, m.p. 63° (also obtained from the acid from Mg 1-methylcyclohexyl chloride and CO₂). Warm NaOH and 10% Na₂CO₃ effect the same change; the latter also gives ~50% of (II). 1-Chlorocyclohexyl Ph ketone, m.p. 59°, prepared similarly, with Na₂CO₃ in Et₂O/12 hr. affords (30–40%) 1-phenylcyclohexane-1-carboxylic acid, m.p. 123° [also obtained by oxidising the corresponding aldehyde (cf. A., 1935, 1240)], and 1-benzoyl-Δ¹-cyclohexene (semicarbazone, m.p. 214°); only the latter is formed with boiling NaOH. The reaction is explained as a semi-benzilic acid change. J. L. D.

Microscopic investigations of polymorphous substances. II. E. LINDPAINTER (Mikrochem., 1939, 27, 21–41; cf. A., 1938, II, 192).—Micro-m.p. determinations show the following nos. of modifications: PhOBz, three, m.p. 69°, 56–5°, 51–52°; benzoyl-*l*-ecgonine, four, m.p. ~202–203°, 179–181°, 130–135°, 100–105°; quinizarin, two enantiotropes, m.p. orange 195°, red 201°; chrysophanic acid, two, m.p. 195°, 190°; coumarin, three, m.p. 68–5°, 64–5°, 55°; gallic acid, two, m.p. ~258–265°, 225–230°; quinal, two, both m.p. 172–5°; morphine hydrochloride, two, m.p. ~295–300°, 280–284°; nipagin [*p*-OH·C₆H₄·CO₂Me], six, m.p. 127°, 116°, 110°, 110°, 109°, 106°; *o*-NO₂·C₆H₄·CHO, two, m.p. 42–42.5°, 39°; *m*-NO₂·C₆H₄·CHO, two, m.p. 56–57°, ~51°; *p*-NO₂·C₆H₄·CHO, two, m.p. 105°, 104–104.5°; phenanthraquinone, two, m.p. 210–211°, 207°; veronal, four, m.p. 190°, >183° but <190°, 183°, 176°; *m*-xylene, two, m.p. 62–63°, ~55°.

J. W. S.

Esterification of highly hindered acids. R. C. FUSON, J. CORSE, and E. C. HORNING (J. Amer. Chem. Soc., 1939, 61, 1290).—Heating the NMe₄ salts of the acids at 200–250° gives 63–90% of Me 2:4:6-trimethyl- and -triethylbenzoate, b.p. 114–115°/5 mm. R. S. C.

Methyl β -resorcyate. S. RANGASWAMI (J. Indian Chem. Soc., 1939, 16, 160).—Me β -resorcyate when freshly prepared (from the acid with MeOH-HCl or MeOH-H₂SO₄) has m.p. 78–80°, unaltered by recrystallisation from MeOH or EtOH; this is the monohydrate. Recrystallised from CHCl₃ it has m.p. 85–110°; this when dried gives the anhyd. ester, m.p. 119–120° (cf. Robinson and Shah, A., 1934, 1346).

J. D. R.

Structure of gossypol. XIX. Synthesis of 2:3-dihydroxy-4-isopropylbenzoic acid. R. ADAMS and M. HUNT. **XX. Synthesis of 3:4-dihydroxy-5-isopropylbenzoic acid.** R. ADAMS, M. HUNT, and B. R. BAKER. **XXI. Synthesis of 3:4-dimethoxy-2-isopropylbenzoic acid and of apogossypolic acid.** R. ADAMS and B. R. BAKER (J. Amer. Chem. Soc., 1939, 61, 1132–1133, 1134–1137, 1138–1142; cf. A., 1939, II, 77).—XIX. 3:1:2-C₆H₃Pr^β(OMe)₂ with LiBu^a in Et₂O-C₆H₆, followed by CO₂ in C₆H₆, gives 2:3-dimethoxy-4-isopropylbenzoic acid, m.p. 72–73°, sublimes at 120°/4 mm., demethylated by 48% aq. HBr to 2:3-dihydroxy-4-isopropylbenzoic acid, m.p. 153°.

XX. 3:4-Dihydroxy-5-isopropylbenzoic acid (I) is synthesised by two methods. Its identity with an acid obtained from gossic and apogossypolic acid by HBr (Adams *et al.*, A., 1938, II, 453) supports the structures of the latter and that of gossypol. 2:1:3-OH-C₆H₃Pr^β-OMe (II) or 1:2:3-C₆H₃Pr^β(OMe)₂ with Ac₂O and AlCl₃ in CS₂ at room temp. gives 4-hydroxy-3-methoxy-5-isopropylacetophenone (57%), m.p. 116°, converted by NaOMe-Me₂SO₄-MeOH into the 3:4-(OMe)₂-ketone, b.p. 135–137°/2 mm., which with KMnO₄ and Na₂CO₃ in aq. COMe₂ yields 3:4-dimethoxy-5-isopropylbenzoic acid (III), m.p. 115°, and thence by 48% HBr (I), m.p. 215°. *o*-OH-C₆H₄-CMe:CH₂ (prep. from *o*-OH-C₆H₄-CO₂Me by MgMeI and distillation), b.p. 201–205°/750 mm., and H₂-Raney Ni in aq. alkali at 2–3 atm. give *o*-C₆H₄Pr^β-OH, converted by Br-CCl₄ into 1:5:2-C₆H₃Pr^βBr-OH, b.p. 150–152°/20 mm. Fuming HNO₃ in AcOH then gives the 3-NO₂-derivative, m.p. 29–30° (lit. 33°), which with Me₂SO₄ and NaOEt-EtOH in PhMe gives 5-bromo-3-nitro-2-methoxyisopropylbenzene, b.p. 137–139°/3 mm., reduced (H₂-Raney Ni in EtOH) to the NH₂-compound, b.p. 134–137°/3 mm. (hydrochloride, m.p. 171–174°). The diazonium sulphate thereof is converted by H₂SO₄-Na₂SO₄-H₂O at 150–170° into a phenol, which yields 5-bromo-2:3-dimethoxyisopropylbenzene, b.p. 120–122°/2 mm. This is converted by a Grignard reaction into (III). Aq. KOH-I oxidises 4:5:3:1-

OH-C₆H₃Pr^β(OMe)-COMe to 4-hydroxy-3-methoxy-5-isopropylbenzoic acid (IV), m.p. 167–169°, also obtained as follows. Br-CCl₄ and (II) give 5-bromo-2-hydroxy-3-methoxyisopropylbenzene, b.p. 113–114°/2 mm., converted by CH₃PhCl and NaOMe-MeOH into the 2-CH₂Ph ether, m.p. 72–73°, which with Mg, a little EtBr, and then CO₂ gives a poor yield of a product, hydrolysed by HCl-EtOH to (IV). The acid, previously (*loc. cit.*) thought to be (III), was (IV), complete methylation of (I) being very difficult. 3:4-(OMe)₂C₆H₃-CO₂Me and MgMeI in Et₂O give 3:4-dimethoxyphenyldimethylcarbinol, m.p. 78° (uncorr.),

also obtained in poorer yield from 3:4-(OMe)₂C₆H₃-COMe and converted by distillation/<1 atm. into a (?) polymeride.

XXI. Synthesis of apogossypolic acid (V) confirms the orientation of the terminal rings of gossypol. 2-Acetoxy-3-methoxyisopropylbenzene [prep. from (II) by Ac₂O], b.p. 118–120°/3 mm., and Br in CCl₄ give the 6-Br-derivative, b.p. 157–168°/10 mm., which by hydrolysis (KOH-EtOH) and methylation (Me₂SO₄-KOH-MeOH-H₂O) affords 6-bromo-2:3-dimethoxyisopropylbenzene, b.p. 122–125°/3 mm. A Grignard reaction then affords 3:4-dimethoxy-2-isopropylbenzoic acid, m.p. 119–121°, yielding with aq. HNO₃ 95% of the 6-NO₂-acid (VI), m.p. 157–159° [obtained (*loc. cit.*) by nitrating (V)]. The derived Me ester, m.p. 89–91°, sublimes at 115°/3 mm., with H₂-Raney Ni in EtOH etc. yields Me 4:5-dimethoxy-6-isopropylanthranilate hydrochloride, m.p. 181–182° (decomp.). A diazo-reaction (CuCN) then gives an oily nitrile, hydrolysed by 10% aq. NaOH to (V) [4:5-dimethoxy-3-isopropylphthalic acid], m.p. 169–170° (decomp.), which is isolated as anhydride, m.p. 92–93°. Hydrogenation (Raney Ni) of (VI) in EtOH-KOH gives the NH₂-acid, which, when sublimed, yields 4:5-dimethoxy-3-isopropylaniline, m.p. 74–75°, sublimes at 100°/15 mm. [Ac₂ derivative, m.p. 84–85° (cf. *loc. cit.*)]. 3:4-(OMe)₂C₆H₃-CMe:CH-CO₂Et [prep. from 3:4-(OMe)₂C₆H₃-COMe, Zn, and CH₂Br-CO₂Et], b.p. 169–170°/4 mm., is hydrolysed and then reduced (H₂-Raney Ni in aq. alkali at 2–3 atm.) to 3:4-(OMe)₂C₆H₃-CHMe-CH₂-CO₂H (60% yield), m.p. 80–82° (lit. 84–85°), which with P₂O₅ in C₆H₆ gives 5:6-dimethoxy-3-methylindanone (85% yield), m.p. 88–90° (uncorr.) (lit. 90–91°). BuNO₂ and conc. HCl in MeOH then give the 2-oximino-derivative (83% yield), m.p. 223–224° (lit. 225–226°), which with SOCl₂ in Et₂O gives a substance, hydrolysed by hot 10% aq. NaOH to 4:5-dimethoxy- α -methylhomophthalic acid, m.p. 173–175° (decomp.) [anhydride, m.p. 126–127°; Me₂ ester, m.p. 57–58°, sublimes at 120°/20 mm.; resists further methylation at C_{6a}]. Similar reactions starting from 3:4-(OMe)₂C₆H₃-COEt, Zn, and CH₂Br-CO₂Et give Et 3:4-dimethoxy-3-ethylcinnamate (78%), b.p. 165°/4 mm., β -3:4-dimethoxyphenyl-n-valeric acid, m.p. 73°, b.p. 185–186°/4 mm., 5:6-dimethoxy-3-ethylindanone (80%), m.p. 92° [2-oximino-derivative (78%), m.p. 218° (decomp.)], 4:5-dimethoxy-, m.p. 157–158° (decomp.) (anhydride, m.p. 85–86°), and (by 48% HBr) 4:5-dihydroxy- α -ethylhomophthalic [α -2-carboxy-4:5-dihydroxyphenyl-n-butyric] acid, m.p. 124–125° (green FeCl₃ colour). M.p. are corr. except where stated.

R. S. C.

Fluorenones and diphenic acids. VII. Ring cleavage of 1:8-, 1:6-, and 3:6-dichlorofluorenones with potassium hydroxide in diphenyl ether. E. H. HUNTRESS and (Miss) M. K. SEIKEL (J. Amer. Chem. Soc., 1939, 61, 1066–1071; cf. A., 1939, II, 264).—Fission of chlorofluorenones by KOH in Ph₂O to acids occurs in only one direction, but, if Cl is *o*-to CO, some lactone formation occurs by replacement of the Cl by OH and rearrangement. Ring-closure of the derived chlorodiphenyl-2-carboxylic acids by

H_2SO_4 at room temp. occurs at both 2 and 6 positions. Coupling diazotised 2:4:1- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$ gives 5:5'-dichlorodiphenic acid and 5:5'-dichloro-2:2'-dicarboxydiphenyl ether, m.p. variable, 310° to 336° (decomp.) [converted by H_2SO_4 into (?) a xanthone, m.p. $346\text{--}347^\circ$ (decomp.)] (cf. Huntress *et al.*, A., 1933, 826). 3:3'-Dichlorodiphenyl-2-carboxylic acid, m.p. $157\text{--}158^\circ$ (lit. $152\text{--}5^\circ$), is obtained by KOH from 1:8-dichlorofluorenone (II) in 50–60% yield and with H_2SO_4 gives 25–35% of (II) and 65–75% of 1:6-dichlorofluorenone (III). 5:3'-Dichlorodiphenyl-2-carboxylic acid, m.p. $154\text{--}155^\circ$, is obtained from 3:6-dichlorofluorenone (IV) (90–92%) and from (III) (50%; sole product), and with H_2SO_4 gives 30–40% of (III) and 60–70% of (IV). The lactone, m.p. $135\text{--}135\cdot5^\circ$, of 3-chloro-2'-hydroxydiphenyl-2-carboxylic acid is obtained as by-product from (II) and KOH, and, with other products, in 3.1% yield from 1:6:2- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{N}_2\text{Cl}$ and PhOH. The lactone, m.p. $173\cdot5^\circ$, of 5-chloro-2'-hydroxydiphenyl-2-carboxylic acid is similarly obtained from (III) or from 1:4:2- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{N}_2\text{Cl}$ and PhOH (10% yield).

R. S. C.

Alkylaminoalkyl esters of aminonaphthoic acids as local anaesthetics. F. F. BLICKE and H. C. PARKE (J. Amer. Chem. Soc., 1939, 61, 1200–1203).—Prep. of 3:1-, 4:1-, 5:1-, and 6:1- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ is outlined. With SOCl_2 at 150° , the acids give 3-, m.p. $137\text{--}139^\circ$, b.p. $205\text{--}206^\circ/12$ mm., 4-, m.p. $95\text{--}96^\circ$, b.p. $208\text{--}210^\circ/17$ mm., 5-, m.p. $132\text{--}134^\circ$, b.p. $214\text{--}217^\circ/18$ mm., and 6-nitro-1-naphthoyl chloride, m.p. $154\text{--}155^\circ$, which with dialkylamino-alcohols (1 mol.) in hot C_6H_6 give the NO_2 -esters. The following are described. β -Diethylaminoethyl, m.p. $211\text{--}213^\circ$, β -di-n-butylaminoethyl, m.p. $169\text{--}170^\circ$, γ -diethylamino-n-propyl, m.p. $203\text{--}204^\circ$, β -, m.p. $149\text{--}150^\circ$, and γ -di-n-butylamino-n-propyl, m.p. $148\text{--}149^\circ$, and γ -dimethylamino- β -dimethyl-n-propyl, m.p. $114\text{--}115^\circ$, 3-nitro-1-naphthoate hydrochlorides, m.p. $148\text{--}150^\circ$, $135\text{--}136^\circ$, $160\text{--}161^\circ$, $113\text{--}114^\circ$, $146\text{--}147^\circ$, and $162\text{--}163^\circ$, respectively. β -Diethylaminoethyl, m.p. $198\text{--}199^\circ$ (lit. $189\cdot8\text{--}190^\circ$), β -di-n-butylaminoethyl, m.p. $76\text{--}78^\circ$, β -, m.p. $139\text{--}140^\circ$, and γ -diethylamino-n-propyl, m.p. $161\text{--}162^\circ$, β -, m.p. $83\text{--}85^\circ$, and γ -di-n-butylamino-n-propyl, m.p. $117\text{--}118^\circ$, γ -dimethylamino-, m.p. $150\text{--}151^\circ$, and γ -diethylamino- β -dimethyl-n-propyl, m.p. $151\text{--}152^\circ$, 4-nitro-1-naphthoate hydrochloride and the derived 4-amino-1-naphthoate hydrochlorides, m.p. $214\text{--}216^\circ$ (lit. 212°), $170\text{--}171^\circ$, $197\text{--}198^\circ$, $184\text{--}185^\circ$, $179\text{--}180^\circ$, $175\text{--}176^\circ$, $219\text{--}221^\circ$, and $184\text{--}186^\circ$ (lit. $187\text{--}188^\circ$), respectively. β -Diethylaminoethyl, m.p. $198\text{--}199^\circ$, β -di-n-butylaminoethyl, m.p. $131\text{--}133^\circ$, β -, m.p. $195\text{--}196^\circ$, and γ -diethylamino-n-propyl, m.p. $193\text{--}194^\circ$, β -, m.p. $120\text{--}121^\circ$, and γ -di-n-butylamino-n-propyl, m.p. $118\text{--}120^\circ$, 5-nitro-1-naphthoate hydrochloride and the derived 5-amino-1-naphthoate hydrochlorides, m.p. $169\text{--}170^\circ$, $178\text{--}179^\circ$, $171\text{--}172^\circ$, $175\text{--}177^\circ$, $157\text{--}159^\circ$, and $159\text{--}160^\circ$, respectively. β -Diethylaminoethyl 6-nitro-, m.p. $184\text{--}185^\circ$, and 6-amino-1-naphthoate hydrochloride, m.p. $169\text{--}170^\circ$. The NH_2 -ester hydrochlorides are local anaesthetics, but some are irritant and insol. in H_2O .

R. S. C.

Synthetic experiments in the equilenin series.

E. BERGMANN (Chem. and Ind., 1939, 465–466).—6:2- $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{MgBr}$ with Et cyclopentanone-2-acetate in Et_2O yields 1-(6'-methoxy-2'-naphthyl)- Δ^1 -cyclohexene-2-acetic acid, m.p. $120\text{--}121^\circ$, and some 6:6'-dimethoxy-2:2'-dinaphthyl, m.p. 284° . Et laevulate with NaOEt in Et_2O affords a compound, $\text{C}_{20}\text{H}_{20}\text{O}_2$, b.p. $154^\circ/0\cdot9$ mm., which gives no coloration with FeCl_3 .

A. LI.

Structure and absorption [spectra] of hydroxy-derivatives of triphenylmethane dyes. Existence of two coloured isomeric forms of phenolsulphonaphthaleins and phenolphthalein. P. RAMART-LUCAS (Compt. rend., 1939, 208, 1312–1314).—The phenolphthaleinsulphonic acids exist in a colourless lactone form, and two coloured forms which have absorption spectra closely resembling those of benzaurin and aurin; hence one isomeride has the fuchsone structure (cf. A., 1939, II, 260). The fuchsone (quinonoid) form of the phenolphthaleins predominates in neutral solution and the other coloured isomeride in alkali. Benzaurin and tetrabromophenolphthalein exist in both coloured isomeric forms, thus negating the views of Meyer (A., 1899, I, 707) and Acrée (A., 1908, I, 423) which seek to explain the isomerism. The two forms have quinonoid structures probably with different valency angles.

J. L. D.

Synthesis of physiologically active lactones.

I. cyclopentyl- and cyclohexyl-succinic acids. Resolution of *dl*-cyclopentylsuccinic acid. S. K. RANGANATHAN (J. Indian Chem. Soc., 1939, 16, 107–113; cf. A., 1938, II, 97).—cyclopentyl bromide (prep. in 88% yield by PBr_3 at -5° to 0° and then at room temp. to 100°), b.p. $133\text{--}134^\circ/680$ mm., $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, and NaOEt give *Et* α -cyclopentylethane- $\alpha\beta$ -tricarboxylate, b.p. $166^\circ/5$ mm., which with hot, conc. HCl yields α -cyclopentylsuccinic acid (I), m.p. $116\text{--}117^\circ$ (anhydride, b.p. $176^\circ/30$ mm.; mono-*p*-toluidide, m.p. 174°), but with alkali gives an impure acid-ester, m.p. 112° . The Et_2 ester, b.p. $120^\circ/2$ mm., of (I) with NaOEt and HCO_2Et in Et_2O gives *Et* α -aldehydo- α -cyclopentylsuccinate, b.p. $150\text{--}154^\circ/3\text{--}5$ mm., which does not react with PhNCO or 10% aq. KOH, is converted by hot, dil. HCl into (I), is unchanged by H_2O at 130° , and with Cu-bronze and $\text{H}_2\text{C}_2\text{O}_4$ in hot H_2O gives β -aldehydo- β -cyclopentylpropionic acid (semicarbazone, m.p. 200°). Similarly are prepared cyclohexyl bromide (88% yield), b.p. $159\text{--}160^\circ/680$ mm., *Et* α -cyclohexylethane- $\alpha\beta$ -tricarboxylate, b.p. $160^\circ/2$ mm., and α -cyclohexylsuccinic acid, m.p. 145° (anhydride, m.p. 42° , b.p. $150^\circ/4$ mm.; mono-*p*-toluidide, m.p. 187°). Resolution of (I) by the brucine salt yields the *d*- and *l*-acids, m.p. 135° , $[\alpha]_D^{25} +17\cdot81^\circ$, $-16\cdot94^\circ$ in COMe_2 .

R. S. C.

$\alpha\alpha$ -Diphenylsuccinic acid. F. SALMON-LEGAGNEUR (Compt. rend., 1939, 208, 1507–1509).— $\text{NaCPh}_2\cdot\text{CN}$ (1 mol.) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (1.5 mols.) affords *Et* β -cyano- $\beta\beta$ -diphenylpropionate (I), m.p. $103\text{--}105^\circ$, converted by $\text{EtOH}\text{--KOH}$ into β -cyano- $\beta\beta$ -diphenylpropionic acid (II), m.p. $183\text{--}184^\circ$, which with boiling conc. HCl gives $\alpha\alpha$ -diphenylsuccinic acid (III),

m.p. 197—199° after softening at 170°. (III) with MeOH-HCl or EtOH-HCl gives *Me*, m.p. 141—143°, or *Et* β -carboxy- $\beta\beta$ -diphenylpropionate (IV), m.p. 144—146°, respectively. These with SOCl_2 -MeOH or SOCl_2 -EtOH give *Me*₂, m.p. 82—83°, or *Et*₂ $\alpha\alpha$ -diphenylsuccinate, m.p. 76—77°, respectively, which are hydrolysed to β -carbomethoxy-, m.p. 183—184°, and β -carbomethoxy- $\beta\beta$ -diphenylpropionic acid, m.p. 137—138°, respectively. (IV) with SOCl_2 followed by treatment with NH_3 affords β -carbethoxy- $\alpha\alpha$ -diphenylpropionamide, m.p. 105—106°, also obtained by hydrolysis (80% H_2SO_4) of (I). Hydrolysis (80% H_2SO_4) of (II) yields β -carboxy- $\alpha\alpha$ -diphenylpropionamide, m.p. 140°. (III) with AcCl or when heated gives $\alpha\alpha$ -diphenylsuccinic anhydride, m.p. 90—91°, easily hydrolysed by aq. Na_2CO_3 , and when boiled with EtOH gives (IV). The NH_4 salt of (III) when heated gives $\alpha\alpha$ -diphenylsuccinimide, m.p. 139°.

J. L. D.

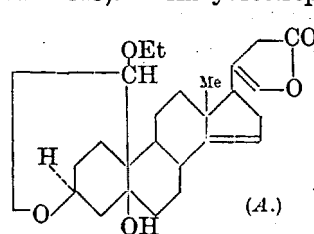
Fused carbon rings. XVII. Stereoisomerism of the perhydrodiphenic acids and an examination of the Blanc rule. R. P. LINSTED and A. L. WALPOLE (J.C.S., 1939, 850—857).—Four of the six possible inactive (four racemic and two *meso*) perhydrodiphenic acids (formulae given) are described. 9-Ketoperhydrophenanthrene, form A (A., 1939, II, 307), is reduced (Ponndorf-Verley) to 9-hydroxyperhydrophenanthrene (I), b.p. 132°/0.5 mm. (acetate, b.p. 127°/1 mm.), dehydrated (KHSO_4) at 200° to do-decahydrophenanthrene, b.p. 127°/13 mm. Oxidation of (I) (the other above three compounds do not react) with HNO_3 (d 1.5 + d 1.42) gives a perhydrodiphenic acid (*trans-trans*), m.p. 202—203° (Ac_2O gives the anhydride, m.p. 135°, which evolves no CO_2 at 350°). 9-Ketoperhydrophenanthrene, form C, m.p. 47—48° (*loc. cit.*), and HNO_3 afford a perhydrodiphenic acid (*cis-trans*) (II), m.p. 243—244° (bath initially at 235°) (anhydride, m.p. 242°), which at 310—320° in N_2 evolves CO_2 and gives a perhydrofluorenone (semicarbazone, new m.p. 216—217°) (cf. Vocke, A., 1934, 189).

[With F. H. SLINGER.] Phenanthraquinone refluxed with H_2O_2 -AcOH gives diphenic acid, hydrogenated (Adams) in AcOH to a perhydrodiphenic acid, m.p. 273—274° (*cis-cis*) (cf. Vocke, *loc. cit.*) (anhydride, m.p. 143°, also + Ac_2O , m.p. 104°), which yields a perhydrofluorene (III) [semicarbazone, m.p. 200—202°, possibly a mixture], and is converted by AcOH-HCl at 200° into an isomeric acid (*cis-trans*) (IV), m.p. 219—220° (anhydride, m.p. 105—106°), which affords (III). *Me* diphenate (V) is similarly reduced to *Me* perhydrodiphenate (VI), m.p. 73°, hydrolysed by KOH-MeOH to (IV). Hydrogenation (Raney Ni) of (V) in methylcyclohexane at 150—300 atm. and 210—215° gives (VI) and an isomeride, hydrolysed to (II). The applicability of the Blanc rule to acids of the adipic series depends on the degree of substitution and on the configuration. The formation of anhydrides and ketones by the Blanc procedure is discussed. The perhydrodiphenic acid, m.p. 213°, of Vocke (*loc. cit.*) has a *trans-trans* configuration.

A. T. P.

Configurational relationships in the steroid series. E. BERGMANN (Chem. and Ind., 1939,

512—513).—"Anhydrostrophanthidin hemiacetal"



(Jacobs and Collins, A., 1924, i, 867) has the structure A and since strophanthidin (I) belongs to the *trans*-decahydronaphthaleneseries its abs. configuration is established. Alkaline isomerisation of (I) to α -isostrophanthidin (II)

involves a configurational change at C_{10} , and rearrangement of the lactonic group; hence α -isostrophanthidic and α -isostrophanthic acid derived from (II) cannot undergo lactol- or lactone-formation and contain OH at C_{10} and CHO (or CO_2H) at C_{10} in *trans* position. (I) is not pptd. by digitonin (III). This precipitability is not exclusively determined by configurational reasons but apparently also by the intactness of the original lactone ring. Probably, however, the cardiac aglucones which are not pptd. by (III) have the same configuration at C_{10} as has (I), whilst uzarigenin (IV) possesses the epimeric arrangement at C_{10} . If this is the case the complete steric arrangement of (IV), gitoxigenin (V), and digitoxigenin (VI) is established since (V) and (VI) have been transformed into α -allocholanolic and α -cholanolic acid, respectively. If digitonide formation in the cardiac aglucone series is ascribed to steric relationships it would seem sp. for the *trans* position between OH at C_{10} and Me at C_{10} . It is difficult to draw definite conclusions with regard to cholesterol (VII) from the known configuration of the 3-OH-dicarboxylic acid of Lettré (A., 1935, 857), but since hydrolysis of the C-Cl linking which produces it from the Cl-acid is accompanied by Walden inversion whilst the way from (VII) to this 3-Cl-acid probably does not give rise to configurational changes at C_{10} , then OH at C_{10} and Me at C_{10} are in *trans* positions in (VII). The fact that substitution of a polar linking by a negative ion is generally (so far as no allylic system is concerned) accompanied by inversion of configuration permits the exact determination of a steric relationship.

H. W.

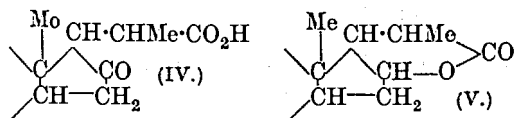
Further colour reactions of sterols in their relationship to constitutive factors. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1939, 22, 666—672).—The behaviour of digitoxigenin and gitoxigenin towards H_2SO_4 and furfuraldehyde- H_2SO_4 is described. In view of the importance of the presence of OH, the reaction with mono- and poly-hydroxy-benzenes has been investigated.

H. W.

Sterols. LIX. Sarsasapogenin derivatives. Deoxysarsasapogenin. LX. Oxidation products of sarsasapogenin. Structure of the C_{22} keto-acid. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 1284—1285, 1285—1287; cf. A., 1939, II, 276).—LIX. Deoxysarsasapogenin (I) [prep. from sarsasapogenone (II) by Zn-HCl-EtOH ; 45% yield from sarsasapogenin (III)], m.p. 214—216°, gives a red ppt. with SeO_2 in C_6H_6 -AcOH, is hydrogenated (PtO_2 ; AcOH; 70°/3 atm.) to dihydrodeoxysarsasapogenin, m.p. 109—110° (unaffected by SeO_2), with Zn-Hg-HCl-EtOH gives

tetrahydrodeoxysarsasapogenin, m.p. 101° [also obtained from (II)], and an *isomeride* (? polymorphous form), m.p. 118°, and with Br and a little HBr in AcOH gives a *Br-derivative*, m.p. 170° (stable to SeO₂). The *semicarbazone*, m.p. 180° (decomp.), of (II) with NaOEt-EtOH at 175–180° gives mainly (III) with 10% of (I).

LX. Sarsasapogenin acetate and CrO₃ give, among other products (cf. lit.), an *acid* (IV), C₂₂H₃₄O₄, m.p. 285–287° (decomp.) [*semicarbazone*, m.p. 204–207° (decomp.)]; *Me ester*, double m.p. 124–126° and 159°, indifferent to H₂-PtO₂, reduced by Na-EtOH or by H₂-PtO₂ in EtOH-Et₂O to a *lactone* (V), C₂₂H₃₄O₃, forms (? polymorphous or stereoisomeric),



m.p. 197–198° and 186–188° (sole product in EtOH-HCl), but giving with Zn-Hg-HCl-EtOH only the *Et ester*, m.p. 163–164°, of (IV). The above structures are probable. R. S. C.

Sterols. LXII. Position of the hydroxyl group in tigogenin and sarsasapogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 1291–1292).—Sarsasapogeninlactone and Br give a *Br-lactone*, C₂₂H₃₁O₃Br, m.p. 194–195°, converted by C₅H₅N into the *keto-lactone*, C₂₂H₃₀O₃, m.p. 213–214°, which is reduced and epimerised by Na-EtOH to *tigogeninlactone*, m.p. 234–235° (oxidised by CrO₃ to a *keto-lactone*, C₂₂H₃₂O₃, m.p. 252–254°). Thus sarsasapogenin and tigogenin have OH at C₃, and differ only in the configuration at C₅. R. S. C.

Nitrones. Condensation of arylnitroso-compounds with di- and tri-nitrotoluenes. I. TÂNĂSESCU and I. NANU (Ber., 1939, 72, [B], 1083–1092).—Nitrones are obtained by the condensation of NO-compounds with substances containing activated Me and their structures are established by the Beckmann transformation with AcCl. Reaction could not be effected between *o*-, *m*-, and *p*-C₆H₄Me·NO₂ and PhNO or *p*-NMe·C₆H₄·NO. *o*-Nitrophenyl-*N*-phenylnitron is converted by AcCl in boiling C₆H₆ or by KOH-EtOH into *o*-NO₂·C₆H₄·CO·NHPh and by boiling Ac₂O-NaOAc into *o*-nitrobenz-*N*-acetanilide, m.p. 112–113°. *m*- and *p*-NO₂·C₆H₄·CH·NPh·O similarly give *m*-NO₂·C₆H₄·CO·NHPh, *m*-nitrobenz-*N*-acetanilide, m.p. 86·5°, and *p*-NO₂·C₆H₄·CO·NHPh and *p*-nitrobenz-*N*-acetanilide, m.p. 137–138°. *p*-NO₂·C₆H₄·CH·NO·C₆H₄·NMe₂·*p* reacts indefinitely with AcCl or PCl₅ but is converted by Ac₂O-NaOAc into *p*-nitrobenz-*N*-acet-*p*-dimethylaminoanilide, m.p. 160° (all nitrones containing ·C₆H₄·NMe₂ appear to behave thus irregularly). 1:2:4-C₆H₃Me(NO₂)₂ and PhNO in presence of Na₂CO₃ or piperidine give (NO₂)₂C₆H₃·CH·NPh·O, m.p. 151°, transformed by AcCl into 2:4-(NO₂)₂C₆H₃·CO·NHPh and by Ac₂O into 2:4-dinitrobenz-*N*-acetanilide, m.p. 182°. 2:4-(NO₂)₂C₆H₃·CH·NO·C₆H₄Me·*p*, m.p. 169°, is isomerised by AcCl in COMe₂ to 2:4-dinitrobenz-*p*-toluidide, m.p. 215°, and converted by Ac₂O-NaOAc at 100° into 2:4-dinitrobenz-*N*-acet-*p*-toluidide. The con-

densation of 1:2:4-C₆H₃Me(NO₂)₂ with *p*-NO·C₆H₄·NMe₂ in C₅H₅N containing I yields 2:4-(NO₂)₂C₆H₃·CH·NO·C₆H₄·NMe₂·*p*, m.p. 194°, whence 2:4-dinitrobenz-*N*-acet-*p*-dimethylaminoanilide, m.p. 206°, also obtained by acetylation of 2:4-dinitrobenz-*p*-dimethylaminoanilide, m.p. 240°. 2:4-(NO₂)₂C₆H₃·CHO and *p*-NMe₂·C₆H₄·NH₂ in C₆H₆ afford 2:4-dinitrobenzylidene-*p*-dimethylaminoanil, m.p. 209·5°. 1:2:4:6-C₆H₂Me(NO₂)₃ and PhNO in EtOH containing Na₂CO₃ or piperidine or in C₅H₅N containing I yield 2:4:6-trinitrophenyl-*N*-phenylnitron, m.p. 147–148° (explosion), which gives 2:4:6-trinitrobenzanilide, m.p. 229–230°, and 2:4:6-trinitrobenz-*N*-acetanilide, m.p. 206–207°. H. W.

Reaction between dimethylaniline and opianic acid. V. M. RODIONOV and A. M. FEDOROVA (Bull. Acad. Sci. U.R.S.S., 1938, Sér. Chim., 951–959).—Opianic acid with NPhMe₂ in the cold yields dimethylaminophenylmeconine (I) (37·5%), m.p. 135–136° (hydrochloride), and the corresponding *Me*₁ ether, m.p. 152–154° [*Na* derivative (+ H₂O)], which gives (I) with *p*-C₆H₄Me·SO₃Me and the *Me Et* ether, m.p. 137°, with *p*-C₆H₄Me·SO₃Et. With boiling NPhMe₂, *Me* opianate (> 30%) is obtained, with small quantities of 3:4:1-C₆H₃(OMe)₂·CHO and 4:3:1-OMe·C₆H₃(OH)·CHO. BzOH with NPhMe₂, either at 1 atm. or under pressure, yields MeOBz (8%). A. Li.

Synthesis of 4-aminocyclohexyl methyl ketone. E. FERBER and H. BRÜCKNER (Ber., 1939, 72, [B], 995–1002).—Reduction (colloidal Pd in HCl or 96% EtOH) of CPhMe yields PhEt. Only small amounts of difficultly isolable products result from the action of Na-Hg on *p*-NH₂·C₆H₄·COMe. Hydrogenation (PtO₂ in EtOH in absence of H⁺) of *p*-NHAc·C₆H₄·OH does not occur at room temp. but leads slowly at 60° to trans- (I), m.p. 164° and cis- (II), m.p. 135°, 4-acetamidocyclohexanol. (I) is hydrolysed by 15% HCl at 120° to trans-4-aminocyclohexanol hydrochloride, m.p. 226–227 (free base, m.p. 110–111°), whilst (II) gives the cis-hydrochloride, m.p. 192–194°, and base, m.p. 78–80°. In H₂O hydrogenation occurs less rapidly than in EtOH but much more rapidly in 96% EtOH containing 1% of AcOH. *p*-NHAc·C₆H₄·COMe in EtOH-PtO₂ absorbs only 1 H₂ and gives a non-cryst. product converted by NaOAc and AcO into α-*p*-acetamidophenylethyl acetate, m.p. 109° (lit. 192°); in 98% EtOH containing 10% of AcOH there is rapid absorption of 4 H₂ with production of a non-cryst. material oxidised by CrO₃ to trans-, m.p. 147–148°, and cis-, m.p. 74–75°, 4-acetamidocyclohexyl *Me ketone* (corresponding semicarbazones, m.p. 217° and 207°, respectively). Either ketone is hydrolysed by 20% HCl at 120° to the same *p*-aminocyclohexyl *Me ketone hydrochloride*, m.p. 173°. Attempts to conduct the hydrolysis without isomerisation were fruitless. H. W.

Constitution of halogenated resaceto- and propio-phenones. D. CHAKRAVARTI and N. CHAKRAVARTY (J. Indian Chem. Soc., 1939, 16, 144–150).—4:1:3-C₆H₃Cl(OH)₂ (I) with AcOH-ZnCl₂ at 145°/3 min., followed by aq. HCl, yields 5-chlororesacetophenone, m.p. 171° (semicarbazone, m.p. 315°), reduced (Clemmensen) to 4-chloro-6-ethylresorcinol

(II), m.p. 84°, which with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ (III) and H_2SO_4 (or P_2O_5) gives 6(or 8)-chloro-5-hydroxy-4-methyl-8(or 6)-ethylcoumarin, m.p. 175° (Ac derivative, m.p. 100°). Similarly from (II) and $\text{CHMeAc}\cdot\text{CO}_2\text{Et}$ is formed 6(or 8)-chloro-5-hydroxy-3:4-dimethyl-8(or 6)-ethylcoumarin, m.p. 183°. 4:1:3- $\text{C}_6\text{H}_5\text{Et}(\text{OH})_2$ (IV) in Et_2O with SO_2Cl_2 yields (II). EtCO_2H with (I) and ZnCl_2 gives 5-chlororesorpiophenone (V), m.p. 90°, which is reduced (Clemmensen) to 4-chloro-6-propylresorcinol, m.p. 63°, and 4-propylresorcinol, m.p. 77° (also formed by reduction of resorpiophenone), which with (III) and H_2SO_4 gives 7-hydroxy-4-methyl-6-propylcoumarin, m.p. 174°. Similarly, (V) and (III) give 6(or 8)-chloro-5-hydroxy-4-methyl-8(or 6)-propylcoumarin, m.p. 185°. 4:1:3- $\text{C}_6\text{H}_5\text{Br}(\text{OH})_2$ and $\text{ZnCl}_2\cdot\text{AcOH}$ give 5-bromoresoracetophenone, m.p. 167° (semicarbazone, m.p. 255°), reduced (Clemmensen) to (IV), which with (III) in the usual way gives 7-hydroxy-4-methyl-6-ethylcoumarin, m.p. 210°. 4-Chloro-orcinol and $\text{CH}_3\text{Ph}\cdot\text{CN}$ in Et_2O with $\text{ZnCl}_2\cdot\text{HCl}$ give a ketone, $\text{C}_{15}\text{H}_{14}\text{O}_3$, m.p. 140°, reduced (Clemmensen) to a substance, m.p. 127°. Similarly, orcinol and $\text{CH}_3\text{Ph}\cdot\text{CN}$ afford a ketone, m.p. 160°, reduced to a substance, m.p. 72°. Clemmensen reduction of coumarin gives a substance, m.p. 235°. J. D. R.

Di- and poly-arylethane series. I. Di-p-xenylethanone [p-xenyl p-xenylmethyl ketone] and its derivatives. E. A. SCHILOV and F. K. JUDIN. **II. Synthesis of $\alpha\beta\gamma\delta$ -tetra-p-xenylbutane- $\alpha\delta$ -dione and of tetra-p-xenylfuran.** F. K. JUDIN (J. Gen. Chem. Russ., 1939, 9, 167—172, 173—175).—I. p-Xenoin and Zn in AcOH yield $\alpha\beta$ -di-p-xenylethanone (I), m.p. 229—230° (oxime, m.p. 173.5—174°), which with Br in CHCl_3 affords α -bromo- (II), m.p. 186—187.5°, and $\alpha\alpha$ -dibromo- $\alpha\beta$ -di-p-xenylethanone, m.p. 181—183°. With HBr (2 hr. at 130—140°) p-xenoin gives (I) and ($p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}$)₂ (III), with PBr_3 the product is (I), and with PBr_5 (III); with SO_2Cl_2 in CHCl_3 α -chloro- $\alpha\beta$ -di-p-xenylethanone (IV), m.p. 164.5—166°, is obtained. (I) and MgPhBr or $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ in Et_2O afford respectively α -phenyl-, m.p. 218.5°, or α -1-naphthyl- $\alpha\beta$ -di-p-xenylethanone, m.p. 188°, dehydrated (HCl in C_6H_6) to α -phenyl-, m.p. 198.5—200°, or α -1-naphthyl- $\alpha\beta$ -di-p-xenylethylene, m.p. 209—214°, respectively.

II. (I) and $\text{Cu}(\text{NO}_3)_2$ in $\text{C}_5\text{H}_5\text{N}$ (6 hr. at the b.p.) yield $\alpha\beta\gamma\delta$ -tetra-p-xenylbutane- $\alpha\delta$ -dione (V), also obtained from (II) or (IV) and Cu in PhMe. (V) and AcCl (2 hr. at 180—200°) yield tetra-p-xenylfuran, m.p. 281—282.5°. R. T.

Condensation of 2-methylnaphthalene and acetyl chloride. G. A. R. KON and W. T. WELLER (J.C.S., 1939, 792—794).—2- $\text{C}_{10}\text{H}_7\text{Me}$, AcCl , and AlCl_3 in PhNO_2 (or, less well, CS_2) at room temp. give 6- and less 8-acetyl-2-methylnaphthalene, b.p. 150—154°/1.5 mm. [semicarbazone, m.p. 181°; no semicarbazone, m.p. 228—230°, is isolated (cf. Dziwowski and Brand, A., 1932, 1250)], oxidised by NaOBr to 2:6- and 2:8- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{CO}_2\text{H}$, respectively, and reduced (Clemmensen) to 2-methyl-6-ethylnaphthalene, m.p. 44—45° [picrate, m.p. 109°; styphnate, m.p. 119°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 116—117°; $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ derivative, m.p. 62°], and 2:8- $\text{C}_{10}\text{H}_6\text{MeEt}$ [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 127—128°;

$\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ derivative, m.p. 77—78°], respectively. 2- $\text{C}_{10}\text{H}_7\text{Me}$ and EtCOCl give (method: Haworth *et al.*, A., 1932, 1024) 6-propionyl-2-methylnaphthalene (semicarbazone, m.p. 224—225°) and no isomeride.

A. T. P.

N-Oximino-ethers. IV. Formation of oximino-ethers in the Ehrlich-Sachs reaction. V. Stereoisomeric N-aryl ethers of oximinophenylacetonitrile. F. BARROW and F. J. THORNEYCROFT (J.C.S., 1939, 769—773; 773—777).—IV. $\text{CH}_3\text{Ph}\cdot\text{CN}$ (I), $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, and aq. $\text{KOH}\cdot\text{EtOH}$ give $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (II), $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CPh}\cdot\text{CN}$ (III), and some oximinophenylacetonitrile N-p-dimethylaminophenyl ether, m.p. 90° (IV). Longer reaction with excess of KOH affords (IV) and $p\text{-NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ [by hydrolysis of (III)]; hydrolysis of (III) with conc. HCl , however, gives BzCN and (II). Similar formation of N-oximino-ethers and (mainly) anils occurs with (I) and $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ or $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NHR}$ ($\text{R} = \text{Me}$ or Et) (with which ether formation is more pronounced). PhNO and (I) in aq. $\text{Na}_2\text{CO}_3\cdot\text{EtOH}$ afford $\text{CN}\cdot\text{CPh}\cdot\text{NPh}$, α - and β -forms of $\text{CN}\cdot\text{CPh}\cdot\text{NPh}\cdot\text{O}$ (V) (cf. A., 1934, 770), azoxybenzene, and NHPhBz . The amide, m.p. 141°, described by Sachs and Bry (A., 1901, i, 272) is probably (V) (β -form). 2:4:1-(NO_2)₂ $\cdot\text{C}_6\text{H}_3\cdot\text{CHO}$ and (II) in EtOH (+ AcOH) give 2:4-dinitrobenzylidene-p-dimethylaminoaniline, green, m.p. 211°, also obtained as the main product from 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ and $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (method: Sachs and Kempf, A., 1902, i, 377); in the latter case some 2:4-dinitrobenzaldoxime N-p-dimethylaminophenyl ether, red, m.p. 193°, is also formed. The mechanism advanced by Schönberg *et al.* (A., 1937, II, 248) is supported.

V. ArNO_2 and Zn in aq. $\text{EtOH}\cdot\text{NH}_4\text{Cl}$ at $\sim 70^\circ$ give the $\text{NHAr}\cdot\text{OH}$, and thence (aq. FeCl_3 at 0—5°) ArNO . $\text{CHPhCl}\cdot\text{CN}$ (VII) and $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}$ in aq. $\text{KOH}\cdot\text{COMe}_2$ give the stereoisomeric oximinophenylacetonitrile α -, m.p. 158°, and β -N-o-tolyl ether, m.p. 117°. Similarly prepared are the analogous ethers: α -, m.p. 134°, and β -N-m-tolyl, m.p. 126°; α -, m.p. 135° (slow heating gives β -form), and β -N-p-tolyl, m.p. 161°; α -, m.p. 143°, and β -N-o-chlorophenyl, m.p. 100°; α -, m.p. 125°, and β -N-m-chlorophenyl, m.p. 156°; α -, m.p. 132°, and β -N-p-chlorophenyl, m.p. 142° ($\alpha \rightarrow \beta$ by slow heating). Configurations are determined by measuring dipole moments. Structural evidence cannot be deduced by comparing m.p. or solubilities in C_6H_6 . (IV) has the β -configuration. A. T. P.

Alkaline fission of naphthyl ketones. L. OLIFSON (J. Gen. Chem. Russ., 1939, 9, 36—40).—Various naphthyl ketones are heated at 250—260° with KOH , when the reaction $\text{CORR}' \rightarrow \text{C}_{10}\text{H}_8 + \text{R}'\text{CO}_2\text{H}$ takes place ($\text{R} = \alpha$ - or $\beta\text{-C}_{10}\text{H}_7$, $\text{R}' = \text{Me}$, Ph , C_{10}H_7 ; $\text{R} = \text{C}_{10}\text{H}_6\text{Et}$, $\text{R}' = \text{Ph}$). When $\text{R}' = \text{Me}$ the reaction $\text{CORR}' \rightarrow \text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H} + \text{R}'\text{H}$ also takes place.

R. T.

Probable existence of three 2:6-dibenzylcyclohexanones. R. CORNUBERT and G. MORELLE (Compt. rend., 1939, 208, 1409—1411; cf. A., 1939, II, 164).—Benzylation of cyclohexanone gives (2%) 2:6-dibenzylcyclohexanone (?) (I), m.p. 105° (cf.

A., 1935, 621), different from the ketones of m.p. 55° and 122° (II) (cf. A., 1934, 297). (I) cannot be converted into either of the other forms. When benzylated all three forms give 2 : 2 : 6 : 6-tetrabenzylcyclohexanone, m.p. 174°. (I) with Pt-H₂ under pressure in Et₂O gives 2 : 6-dihexahydrobenzylcyclohexanol (an oil) [phenylurethane, m.p. 132—134°, different from that obtained similarly from (II)].

J. L. D.

Conversion of a C₅ into a C₆ ring by pinacolic dehydration. R. CALAS (Compt. rend., 1939, 208, 1413—1415).—Me *trans*-3-methylcyclopentanol-1-carboxylate with MgMeI gives 3-methyl-1- α -hydroxyisopropylcyclopentanol, m.p. 57°, converted by aq. H₂C₂O₄ into 2 : 2 : 4-trimethylcyclohexanone (65%), b.p. 80°/23 mm. (semicarbazone, m.p. 212°) (also obtained by methylating 2 : 4-dimethylcyclohexanone), *cis*- (~35%) (semicarbazone, m.p. 154°) and a little *trans*-1-acetyl-1 : 3-dimethylcyclopentane (semicarbazone, m.p. 110°), and a very small amount of a diene hydrocarbon, b.p. 151—152°/760 mm., which polymerises readily. The ketones are first separated as oximes and then by fractional crystallisation of the semicarbazones.

J. L. D.

Preparation of cyclic ketones by ring-enlargement. E. P. KOHLER, M. TISHLER, H. POTTER, and H. T. THOMPSON (J. Amer. Chem. Soc., 1939, 61, 1057—1061).—Cyclic ketones are prepared in quantity by ring-enlargement by one CH₂ by adding NO-NMe·CO₂Et in MeOH to a lower cyclic ketone and Na₂CO₃ in MeOH at 20—25°. Some introduction of >1 CH₂ occurs. Other conditions give no better results. The yield is 63% for cycloheptanone (I), 45% for cyclooctanone, 20% for cyclo-nonanone and -decanone (very slow reaction), but increases for C₁₁-ketones. cycloHexanone gives also MeEtCO₃, 15% of epoxymethylenecyclohexane, b.p. 148°, m.p. —38.3° to —40.5° (hydrolysed to the glycol, m.p. 74°), Δ^1 -cyclohexenylcarbinol, b.p. 92—94°/15 mm. (phenylurethane, m.p. 96°; hydrogenated to the known cyclohexylcarbinol), and (?) dicyclohexyldioxan, b.p. 147.5—148°/11 mm. H₂-Raney Ni at 150—165°/33—133 atm. hydrogenates (I) in EtOH quantitatively to cycloheptanol, b.p. 185—186°, converted (distillation with 2-C₁₀H₇·SO₃H) in 80% yield into cycloheptene, b.p. 114.38°, the oily, unstable dibromide of which with anhyd. NHMe₂, first in CHCl₃ at 0° to —5° and then in CHCl₃-C₆H₆ at 100°, gives Δ^2 -cycloheptenyldimethylamine (II) (57—62%), b.p. 184—187°, and 1-bromocycloheptene, b.p. 66.5—67.5°/13 mm., 191°/760 mm. The methobromide, m.p. 192—193° (decomp.), of (II) and aq. KOH give (distillation in N₂) 85—90% of cycloheptadiene (III), b.p. 121.52°/758.3 mm., m.p. —110.42°, the dibromide from which with quinoline at 140° in N₂ yields 66% of cycloheptatriene, b.p. 115.5°/760 mm., m.p. —79.49° [maleic anhydride adduct, m.p. 102—104°, formed in hot xylene, hydrolysed by 10% Na₂CO₃ to the dicarboxylic acid, m.p. 170—174° (decomp.), and hydrogenated (PtO₂) in AcOH-Ac₂O to the H₄-derivative (IV), m.p. 71—73°]. With Na₂CO₃, (IV) gives an acid, m.p. 146—147° (decomp.), but with conc. HCl at 180° yields a *trans*-acid, m.p. 205—210°. (III) gives similarly (cf. Koch, Diss., Kiel, 1932) the

U (A., II.)

maleic anhydride adduct, m.p. 110—111°, and its H₂-derivative, m.p. 156—157° [derived *cis*-, m.p. 132—134° (decomp.), and *trans*-acid, m.p. 215—220°]. cycloHeptanone yields cyclooctanone, b.p. 115—115.5°/60 mm., m.p. 43.8° (semicarbazone, m.p. 168—169°), with smaller amounts of epoxymethylenecycloheptane, b.p. 160—173°, and higher-boiling material. H₂-Raney Ni then gives cyclooctanol, b.p. 111.3—111.7°/25 mm., m.p. 25.06°, converted by 2-C₁₀H₇·SO₃H into cyclooctene, b.p. 143.8—144.5°/773 mm., the dibromide of which with NHMe₂ gives only a trace of amine and 70% of 1-bromocyclooctene, b.p. 97—98°/23 mm. 1 : 2-Dichlorocyclooctane, b.p. 130.4—130.6°/25 mm., m.p. —5°, gives similarly almost entirely 1-chlorocyclooctene, b.p. 77—78°/19 mm. cycloNonanone, b.p. 103.5—104.2°/22 mm., m.p. 31—31.5° (semicarbazone, m.p. 183—185°), and a little cyclodecanone, b.p. 87.5—88°/8 mm., m.p. 20—22° (semicarbazone, m.p. 210—211°), are obtained from cyclooctanone (cf. Adamson *et al.*, A., 1939, II, 116).

R. S. C.

Inter- and intra-molecular acylations with hydrogen fluoride. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1939, 61, 1272—1281).—Commercial anhyd. HF at room temp. is often an advantageous reagent for intramolecular ring-closure of γ -arylbutyric and β -arylpropionic acids. Experiments are detailed for γ -phenyl-, γ -3-acenaphthyl-, and γ -4-methoxy-3-diphenylbutyric acid (gives 1-keto-5-methoxy-8-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 120—120.5°, not obtainable by other methods), and β -phenylpropionic acid; success is recorded without details for 6 similar acids. The reaction failed for a β -aroylpropionic acid and for *o*-COPh·C₆H₄·CO₂H. I- β - α' -Naphthylethylcyclohexanol gives a product, dehydrogenated by Se to chrysene (poor yield). Anthrone is obtained in 82% yield from *o*-CH₂·Ph·C₆H₄·CO₂H, and *o*- α -C₁₀H₇·CH₂·C₆H₄·CO₂H gives 68—75% of pure 1 : 2-benz-10-anthrone, whence MgMeCl gives 56% of 10-methyl-1 : 2-benzanthracene, m.p. 140—141° [separated by adsorption on Al₂O₃ from a little (?) 1 : 2-benz-10-anthranol]. 3-Methoxy-1 : 2-benz-10-anthrone is similarly prepared in 58% yield. HF does not cause ketone formation from C₆H₆ and *o*-C₆H₄(CO₂H)₂ or BzOH, C₁₀H₈ and succinic anhydride (I) or crotonic acid (II), phenanthrene and CH₂Cl·CH₂·COCl or AcCl, 9 : 10-dihydrophenanthrene and AcCl, anthracene and CH₂Cl·COCl, or 1 : 2-benzanthracene and H₂C₂O₄. Quinol and BzOH merely give the monobenzoate. Acenaphthene (III), however, readily reacts to give ketones; with BzOH it gives 62% and with BzCl 87% of 3-benzoylacenaphthene; (I) yields mainly γ -keto- γ -3- with some γ -keto- γ -1-acenaphthylbutyric acid (IV). With AcOH, (III) gives 25% of 1-acetoacenaphthene (V), m.p. 104.7—105.2°, b.p. 154—155°/1 mm., and some of the 3-isomeride (VI), forms, m.p. 59—59.5° and 69.5—70° (lit. 75° only) [picrate, m.p. 97.5—98°; C₆H₃(NO₂)₃ derivative, m.p. 112—113°]. With I-KI in aq. dioxan (V) gives acenaphthene-1-carboxylic acid, m.p. 256—257°; (V) is also obtained from the Me ester of (IV) by heating its Br-derivative, m.p. 103° (decomp.), with alcoholic alkali. AlCl₃, AcCl, and (III) in PhNO₂ yield mainly (VI) with some (V).

With HF, (II) and (III) give 62% of 1'-keto-3'-methyl- Δ^4 -cyclopenteno-4':5'-2:3-acenaphthene (VII), m.p. 167—167.5°, the structure of which is proved as follows. It is indifferent to Br-CHCl₃ and KMnO₄-COMe₂. CHMe:CH-COCl, (III), and AlCl₃ in CS₂ at 10—15° give 23% of 3-crotonylacenaphthene, m.p. 63—63.5° [oxidised by KMnO₄ in NaOH to 1:4:5-CO₂H:C₁₀H₅(CO)₂O], which with HF yields 50% of (VII). Zn-Hg-HCl-PhMe-H₂O-AcOH and (VII) give 85% of 1'-methyl- Δ^4 -cyclopenteno-4':5'-2:3-acenaphthene, m.p. 38—38.5° [C₆H₃(NO₂)₃ derivative, m.p. 113—114°], giving no cryst. product when dehydrogenated by Se or Pd-C. With anhyd. Na₂Cr₂O₇ in AcOH at <100° and then at the b.p., (VII) gives 29% of 2-acetonaphthalene-1:4:5-tricarboxylic acid (VIII), m.p. 160° (instantaneous) or 189—191° (slow heating), the anhydride, m.p. 217—218° (Me ester, m.p. 261—262°, obtained from the acid by CH₂N₂-Et₂O), of which with basic Cu carbonate in hot quinoline yields 3-aceto-1:8-naphthalic anhydride, m.p. 217.5—218.5°. NaOCl oxidises (VIII) to naphthalene-1:2:4:5-tetracarboxylic acid, m.p. (impure) 250° (instantaneous), 262—262.5° (slow heating) (dianhydride, m.p. 262.5—263°; Me₂ ester anhydride, m.p. 219.5—220.5°, obtained from the acid by CH₂N₂-Et₂O). Hydrindene and perinaphthan also condense with BzCl or AcOH in presence of HF. M.p. are corr. R. S. C.

Syntheses of polycyclic compounds related to the sterols. VII. Cyclisation of γ -5-methoxy-1-naphthylbutyric acid. G. A. R. KON and H. R. SOPER (J.C.S., 1939, 790—792; cf. A., 1936, 465).— γ -5-Methoxy-1-naphthylbutyric acid (I) and SnCl₄ in PhMe at 100° (bath) give (results are variable) 1-keto-8-methoxy-1:2:3:4-tetrahydrophenanthrene (II), m.p. 137°, converted by MgMeI, followed by dehydrogenation by Pd-C at 300—330°, into 8-methoxy-1-methylphenanthrene, m.p. 121—121.5° [picrate, m.p. 153—154°; s-C₆H₃(NO₂)₃ compound, m.p. 177—178°; styphnate, m.p. 179—180°]. 7-Keto-4-methoxy-7:8-dihydrohomophenalene, m.p. 88—89° (compound C₁₅H₁₄O₂, loc. cit.), is oxidised (Na₂Cr₂O₇-AcOH) to 4:1:8-OMe-C₁₀H₅(CO₂H)₂, also obtained by oxidation of 3-methoxyacenaphthene, m.p. 66°, b.p. 174°/13 mm. (from 3-aminoacenaphthene by the diazo-reaction and subsequent methylation). A. T. P.

Syntheses in the sterol and sex hormone group. III. Synthesis of 7-hydroxy-3'-keto-3:4-dihydro[cyclopenteno-1':2'-1:2-phenanthrene]. C. K. CHUANG, C. M. MA, Y. L. TIEN, and Y. T. HUANG (Ber., 1939, 72, [B], 949—953).—Condensation of γ -6-methoxy-1-naphthylbutyryl chloride with Et₂ sodioacetyl succinate (I) followed by hydrolysis of the product affords γ -keto- ζ -6-methoxy-1-naphthylheptioic acid, m.p. 80—81° (after purification through the semicarbazone, m.p. 166—167°). The Me ester is condensed by NaOEt in Et₂O to the non-cryst. 2- β -6'-methoxy-1'-naphthylethylcyclopentane-1:3-dione, converted by P₂O₅ into 3'-keto-7-methoxy-3:4-dihydro[cyclopenteno-1':2'-1:2-phenanthrene] (dehydronorequilenin Me ether), m.p. 210—211° (semicarbazone, decomp. ~310°). This is demethylated by AcOH-HBr (*d* 1.49) at 110° to the

7-OH-derivative, m.p. 319° (decomp.) in bath preheated to 315°, and reduced (Clemmensen) and then dehydrogenated (Se at 300—320°) to 7-methoxy-[cyclopenteno-1':2'-1:2-phenanthrene], m.p. 133—134°. γ -6-Methoxy-1-naphthyl- α -methylbutyryl chloride appears to react normally with (I) or with Et₂ sodio- α -acetylglutarate but hydrolysis of the product gives essentially the original acid in each case. H. W.

Ethyl bisindanedionecarboxylate. G. WANAG (Ber., 1939, 72, [B], 973—976).—A dimeric product could not be obtained by the action of Et 2-chloro- with Et sodio-indane-1:3-dione-2-carboxylate (I). Et₂ bisindanedionecarboxylate (diphthalylsuccinate) (II), m.p. 211°, is obtained in 64% yield by the oxidation of (I) with PbO₂ (prepared according to Gattermann) in AcOH at room temp. (II) reacts readily with NHPH-NH₂ but gives only amorphous materials with varying N content. With NH₂Ph in absence of solvent resins result; condensation does not occur in EtOH but in presence of AcOH there is ready formation of the dianil, C₃₈H₂₈O₆N₂, m.p. 221—222°. Protracted action of an excess of NH₂Ph leads to the production of some phthalanil, m.p. 207°; the di-*p*-tolil has m.p. 256°. Reaction does not take place with NHPHMe or NPhMe₂. (II) is very stable towards acids but the protracted action of boiling conc. HCl or cold conc. H₂SO₄ leads to some dihydroxynaphthacenequinone. (II) is very sensitive to alkali. H. W.

Heteropolarity. XXXV. Action of nitroso-dimethylaniline on phenyclone. W. DILTHEY and H. PASSING (J. pr. Chem., 1939, [ii], 153, 35—53; cf. A., 1938, II, 494).—Phenyclone is regularly obtained from pure phenanthraquinone and (CH₃Ph-CO)₂ by a limited amount of alkali in pure EtOH (cf. A., 1935, 1241). With *p*-NO-C₆H₄-NMe₂ in C₅H₅N and N₂ it gives CO and 9:10-dibenzoylphenanthrenemono-*p*-dimethylaminoanil (I), yellow, m.p. 217—218° (decomp.); in presence of 5% of C₅H₅N.HCl some 3:6-diphenyl-2-*p*-dimethylaminophenyl-4:5-oo'-diphenyleneisooxazine (II), m.p. 351—352°, also results. Steric considerations show that the initial polycyclic adduct, being unstable, loses CO and forms (I) by ring-fission, and that (II) is a secondary product derived from (I). Structures are proved by the following reactions. HCO₂H, AcOH, or H₂S in hot C₅H₅N converts (I) into (II); AcOH (and other fatty acids) also causes some hydrolysis. NaOMe-MeOH or H₂O₂-NaOH are without action on (I), but H₂O₂ in HCO₂H gives 9:10-dibenzoylphenanthrene (III) and *p*-NO₂-C₆H₄-NMe₂, possibly by way of (II) which is similarly oxidised. (I) gives a yellowish-red mono-, m.p. 220—221° (decomp.), and yellow (?) di-hydrochloride, amorphous, a red mono-, m.p. 273° (decomp.) (addition of HClO₄ to C:N to give CH-N⁺), and yellow di-perchlorate, m.p. 239—241° (decomp.), a monopicrate, m.p. 194—196° (decomp.), and an oxime, m.p. 340—341° (slow heating) or double m.p. 250° and 339—340° (rapid heating); warm C₅H₅N reconverts the salts into (I). With MgPhBr in PhMe (I) gives 9- α -*p*-dimethylaminoanilobenzyl-10- α -hydroxybenzhydrylphenanthrene, m.p. 283—284° (decomp.) [mono-, m.p. 308—309° (decomp.), and di-

perchlorate, m.p. 297—300° (decomp.); *monopicate*, m.p. 264—266° (decomp.). (II) gives a *perchlorate*, m.p. 292—293° (decomp.), and *picrate*, m.p. 211—212° (decomp.). $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{HCl}$ (not the free base) and (III) in hot $\text{C}_5\text{H}_5\text{N}$ under N_2 give (II).

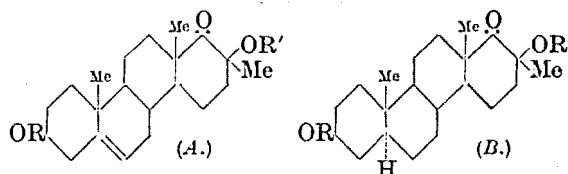
R. S. C.

Estrone and estradiol benzyl ethers.—See B., 1939, 665.

Furfuraldehyde [colour] reactions of vitamin- D_2 , hormones of the adrenal cortex, the corpus luteum, and the androstereone and testosterone group and their relationships to constitutive factors. G. WOKER and I. ANTENER (Helv. Chim. Acta, 1939, 22, 511—519; cf. A., 1939, II, 156).—The opening of ring B, occurring during the activation of egosterol to vitamin- D_2 , causes profound change in the H_2SO_4 -furfuraldehyde reaction and to a smaller degree in the H_2SO_4 reaction whereas the complete removal of the long side-chain is of much less importance. Great change is induced by the saturation of the double linking in dehydroandrostereone but the *cis*- or *trans*-configuration of the product of the change has also considerable influence. The position of the double linkings, apart from their no., is of great significance. The presence of at least 1 OH appears essential for an intense colour reaction. H. W.

Steroids and sex hormones. LII. Constituents of the adrenal cortex and related substances. XXIV. Constitution of the ketones formed by treating 17-hydroxy-17-acetylenyl-androstane derivatives with acetic acid in presence of mercury oxide and boron fluoride. L. RUZICKA, K. GÄTZI, and T. REICHSTEIN (Helv. Chim. Acta, 1939, 22, 626—640; cf. A., 1938, II, 413).—Addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$ to 17-acetylenyl-androstane-3-*trans*-17(α)-diol 3-monoacetate in $\text{AcOH}\cdot\text{Ac}_2\text{O}$ containing HgO gives a *diacetate* (I), $\text{C}_{25}\text{H}_{38}\text{O}_5$, m.p. 227—229°, $[\alpha]_D^{25} 0.0 \pm 0.2^\circ$ in COMe_2 (also obtained from 17-acetylenyl-3-*trans*-17(α)-diacetoxo-androstane and -androstene), and a *diacetate* (II), $\text{C}_{25}\text{H}_{38}\text{O}_5$, m.p. 222—224°, $[\alpha]_D^{25} -7.9 \pm 2^\circ$ in COMe_2 . (I) appears indifferent to H_2 (PtO_2 in AcOH) or to CrO_3 in AcOH . (I) is hydrolysed by $\text{KOH}\cdot\text{MeOH}$ to the (OH)₂-ketone (III), $\text{C}_{21}\text{H}_{34}\text{O}_3$, m.p. 305—306°, or 274—275° (vac.); the corresponding *monoacetate* (IV), m.p. 244—244.5°, $[\alpha]_D^{25} -31.3 \pm 2^\circ$ in COMe_2 , is hydrogenated (PtO_2 in AcOH) and then acetylated to a *monoacetate*, m.p. 251—251.5°, and a *diacetate*, $\text{C}_{25}\text{H}_{40}\text{O}_5$, m.p. 263.5—264° (which contains a *tert*.-OH); the latter substance is hydrolysed to the *triol*, m.p. 303—305°. (III) is oxidised by CrO_3 in AcOH at room temp. to the (CO)₂-acid, $\text{C}_{21}\text{H}_{32}\text{O}_4$, m.p. 226—228° (*Me* ester, m.p. 106—107°). Similarly (IV) gives an *acid*, $\text{C}_{23}\text{H}_{34}\text{O}_5$, m.p. 115—117° (*Me* ester, m.p. 106—106.5°, and its *semicarbazone*, m.p. 228—232°). (II) is hydrolysed to a (OH)₂-ketone (V), $\text{C}_{21}\text{H}_{34}\text{O}_3$, m.p. 205—206° (opaque at 110°); its *diacetate*, $\text{C}_{25}\text{H}_{38}\text{O}_5$, m.p. 161—162°, $[\alpha]_D^{25} -34.8 \pm 2^\circ$ in COMe_2 , is reduced (PtO_2 in AcOH) and then acetylated ($\text{C}_5\text{H}_5\text{N}\cdot\text{Ac}_2\text{O}$ at room temp.) to the *triacetate*, $\text{C}_{27}\text{H}_{42}\text{O}_6$, m.p. 204—205°, which yields the *triol*, m.p. 298—300°. Oxidation of (V) gives a neutral substance, m.p. 203—205° (not identical with *allopregnanedione*), and an *acid*, m.p. 283—292°. All m.p. are corr. H. W.

Steroids and sex hormones. LIII. Hydration of 17-hydroxy-17-acetylenyl derivatives of the androstane and androstene series. L. RUZICKA, M. W. GOLDBERG, and F. HUNZIKER (Helv. Chim. Acta, 1939, 22, 707—716).—Previous results (A., 1939, II, 76) are modified. Δ^5 -Acetylenyl-androstene-3-*trans*-17-diol and $\text{Hg}(\text{OAc})_2$ in EtOH or, preferably, in EtOAc at room temp. and decomp. of the product with H_2S give the compound A ($\text{R} = \text{H}$; $\text{R}' = \text{Ac}$), m.p. 221—222°, $[\alpha]_D -53 \pm 1^\circ$ in dioxan, hydrolysed to the *alcohol*, m.p. 275—277°, $[\alpha]_D -113 \pm 3^\circ$ in dioxan, obtained by the $\text{BF}_3\cdot\text{HgO}$ method.



Similarly, 17-acetylenyl-androstanediol affords the *ketone acetate* (B, $\text{R} = \text{H}$; $\text{R}' = \text{Ac}$), m.p. 202—204°, $[\alpha]_D \pm 0^\circ \pm 2^\circ$ in dioxan, whilst under similar conditions its *diacetate* yields the *diacetate* (B, $\text{R} = \text{R}' = \text{Ac}$), m.p. 227—229°, $[\alpha]_D -3.4 \pm 1^\circ$ in dioxan, hydrolysed to the (OH)₂-ketone (B, $\text{R} = \text{R}' = \text{H}$), m.p. 274—275° when rapidly heated (when slowly heated it is converted into a modification, m.p. 305°), $[\alpha]_D -30 \pm 10^\circ$ in dioxan (*oxime*, m.p. 248—249°; *monoacetate*, m.p. 244—245°, $[\alpha]_D -31 \pm 1^\circ$ in dioxan). 17-Acetylenyltestosterone gives the *acetoxydiketone* (I) (C, $\text{R} = \text{Ac}$), m.p. 198—200°, $[\alpha]_D +66 \pm 1^\circ$ in dioxan, hydrolysed to the *OH-diketone* (C, $\text{R} = \text{H}$), m.p. ~280°, $[\alpha]_D +47 \pm 2^\circ$ in dioxan. (I) is also obtained from 17-acetylenyltestosterone acetate. All m.p. are corr. (vac.). H. W.

New syntheses in the sterol series. G. EHRLHART, H. RUSCHIG, and W. AUMÜLLER (Angew. Chem., 1939, 52, 363—366).—Under definite conditions 3-hydroxybisanthracenic acid is very smoothly degraded (Curtius) to 3-hydroxyternorcholenylamine (I), converted by HNO_2 into pregnenediol, which is oxidised to progesterone (II). Preferably (I), its *O*-Ac derivative, or 3-ketoternorcholenylamine is converted by HOCl into the stable, cryst. chloroamine; this with alkali yields the ketimine, which is hydrolysed by acid to (II). This reaction with HOCl appears to be general for higher amines. Deoxycholic acid is transformed (Grignard and double degradation) into 3:12-dihydroxybisanthracenic acid, acetylated and degraded (Curtius) to 3:12-diacetoxysterorcholenylamine; this is converted by successive treatment with HOCl and hydrolysis into 3:12-dihydroxypregnanone. The 3:12-Ac₂ derivative of this is partly hydrolysed to 3-hydroxy-12-acetoxypregnanone, which is oxidised and brominated to 4-bromo-3-keto-12-acetoxypregnanone; this is transformed by loss of HBr followed by cautious hydrolysis into 12-hydroxypregesterone. Pregnenolone is converted by the Beckmann transformation into 3-hydroxy- α -tiocholenylamine, oxidised to 3-keto-

ætiocolenylamine, which is transformed (HOCl etc.) into androstenedione. Acetylpregnenolone is oxidised by $\text{Pb}(\text{OAc})_4$ to 3:21-diactoxypregnenone. Progesterone is converted similarly into deoxycorticosterone acetate; by use of the corresponding Pb salt, the propionate, benzoate, palmitate, etc. are obtained. Deoxycorticosterone has m.p. 138–140° and 152–154° after resolidification; it is polymorphous.

H. W.

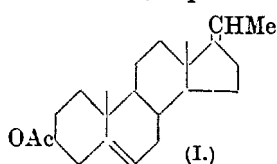
epi- Δ^5 -Pregnen-3-ol-20-one. A. BUTENANDT and A. HEUSNER (Ber., 1939, 72, [B], 1119–1121).— Δ^5 -Pregnen-3:20-dione is reduced (Raney Ni in EtOH) to Δ^5 -pregnenolone (removed by pptn. with digitonin) and epi- Δ^5 -pregnen-3-ol-20-one, m.p. 148–152° (softens at 144°), $[\alpha]_D^{20} +54.5^\circ$ in EtOH (acetate, m.p. 147°, $[\alpha]_D^{20} +57.2^\circ$).

H. W.

Steroids and sex hormones. LIV. Addition of oxygen to $\Delta^{4,17}$ -21-acetoxypregnadien-3-one. L. RUZICKA and P. MÜLLER (Helv. Chim. Acta, 1939, 22, 755–757).—17-Vinyltestosterone is obtained in excellent yield by partial hydrogenation ($\text{Pd}-\text{CaCO}_3$ in $\text{C}_5\text{H}_5\text{N}$) of 17-acetylenyltestosterone. $\text{o}-\text{CO}_2\text{H}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ transforms $\Delta^{4,17}$ -21-acetoxypregnadien-3-one (I) in Et_2O into Δ^4 -17:20-oxido-21-acetoxypregnen-3-one (m.p. 125° (corr.), $[\alpha]_D +99^\circ \pm 1^\circ$ in dioxan. (I) is converted by OsO_4 in Et_2O followed by Na_2SO_4 in $\text{EtOH}-\text{H}_2\text{O}$ into Δ^4 -17(β):20:21-trihydroxypregnen-3-one, m.p. 190° (corr.), $[\alpha]_D +62.6 \pm 1^\circ$ in dioxan.

H. W.

Transformation of dehydroandrosterone into 17-isoprogesterone and progesterone. A. BUTENANDT, J. SCHMIDT-THOMÉ, and H. PAUL (Ber., 1939, 72, [B], 1112–1118).—17-Ethylandrosterone-3:17-diol is converted by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 20° into the 3-monoacetate, m.p. 167–168°, transformed by POCl_3



in boiling $\text{C}_5\text{H}_5\text{N}$ into the substance (I), m.p. 140°. This is converted by the successive action of OsO_4 in Et_2O and Na_2SO_3 into Δ^5 -pregnene-3:17:20-triol (II), m.p. 227°, $[\alpha]_D^{20} -75^\circ$ in

EtOH; the unpurified product is converted by Ac_2O in $\text{C}_5\text{H}_5\text{N}$ at 20° into two stereoisomeric 3:20-diactates (III), m.p. 182°, $[\alpha]_D^{20} -74^\circ$ in EtOH, and m.p. 152–153°, $[\alpha]_D^{20} -36^\circ$ in EtOH. The former is hydrolysed by aq. KHCO_3 to a pregnenetriol, m.p. 241° (slight decomp.), $[\alpha]_D^{20} -102^\circ$ in EtOH, whereas the latter affords (II). Either triol is converted by $\text{Pb}(\text{OAc})_4$ in AcOH to dehydroandrosterone. At 120°/0.01 mm., (III) (m.p. 182°) and Zn dust afford 17-isopregnen-3-ol-20-one acetate, m.p. 169–171°, $[\alpha]_D -126^\circ$ in EtOH, hydrolysed (aq. KHCO_3) to 17-isopregnen-3-ol-20-one, m.p. 170–172°, $[\alpha]_D -136^\circ$ in EtOH. This is oxidised by $\text{Al}(\text{OPr}^i)_3$ in PhMe-cyclohexane to 17-isoprogesterone, m.p. 145° after softening at 142°, $[\alpha]_D^{20} \pm 0^\circ$ in EtOH, isomerised (boiling HCl-EtOH) to progesterone, m.p. 127–128°, $[\alpha]_D +187^\circ$ in EtOH. H. W.

Methyl 17(α)-hydroxy-3-ketoætiolochololate and methyl androstane-17(α)-ol-3-one 17-acetate. K. GÄTZI (Helv. Chim. Acta, 1939, 22, 753–754).—Oxidation (CrO_3 in AcOH) of Me 3(β):17(α)-dihydroxyætiolochololate gives Me 17(α)-hydroxy-

3-ketoætiolochololate, m.p. 228–230° (corr.). Me Δ^5 -3(β):17(α)-dihydroxyandrostene 17-acetate is reduced (PtO_2 in AcOH) to Me 3(β):17(α)-dihydroxyandrostane 17-acetate, m.p. 179–181° (corr.), which is oxidised by CrO_3 in AcOH at room temp. to Me androstan-17(α)-ol-3-one 17-acetate, m.p. 119.5–120.5° (corr.). Neither ester is identical with that described by Ruzicka *et al.* (A., 1939, II, 327).

H. W.

Oxidation of cholesterol and trans-dehydroandrosterone with osmium tetroxide. M. I. USCHAKOV and A. I. LIUTENBERG (J. Gen. Chem. Russ., 1939, 9, 69–72; cf. A., 1937, II, 458).—Cholesterol in Et_2O and OsO_4 (42 hr. at room temp.) yield *cis*-cholestane-3:5:6-triol (3:6-diactate, m.p. 188–189°), oxidised by CrO_3 in AcOH (23 hr. at room temp.) to *cis*-cholestan-5-ol-3:6-dione. Dehydroandrosterone and OsO_4 similarly give *cis*-androstane-3:5:6-triol-17-one [3:6-diactate, m.p. 248.5–249.2° (corr.)]. Δ^4 -Androstene-3:6:17-trione is reduced (Zn in AcOH) to androstane-3:6:17-trione, m.p. 191–192°.

R. T.

Photochemical transformation of $\alpha\beta$ -unsaturated steroid ketones under the influence of ultraviolet light. A. BUTENANDT and A. WOLFF (Ber., 1939, 72, [B], 1121–1123).—The photochemical change causes alteration in the absorption spectrum and disappearance of 3-CO recognisable by the ordinary reagents; the product is not an $\alpha\beta$ -unsaturated ketone. Cholestenone gives a product, $\text{C}_{27}\text{H}_{48}\text{O}_2$, gradual decomp. >360°, $[\alpha]_D^{20} +36.2^\circ$ in CHCl_3 . Substances, $\text{C}_{27}\text{H}_{48}\text{O}_4$, slow decomp. >340°, $[\alpha]_D^{20} +107^\circ$ in CHCl_3 [dioxime, m.p. 390–400° after gradual decomp. at >280°, formed from CO group at C_{20}], and $\text{C}_{27}\text{H}_{48}\text{O}_6$, m.p. 350–355° after gradual decomp. >300°, are derived from progesterone and testosterone, respectively.

H. W.

Halogenation in the anthraquinone series. F. H. DAY (J.C.S., 1939, 816–818).—K anthraquinone-1-sulphonate and Br-HBr- H_2O at 250° for 24 hr. give 1-bromoanthraquinone. The 1:5- and 1:8-disulphonates give small yields only of (?) dibromoanthraquinones. β - SO_3H groups are not replaced at 260°. Anthraquinone-1-carboxylic acid and aq. NaClO_3 -HCl, or Br- H_2O , at 200°, afford 1-chloro- or 1-bromo-anthraquinone, respectively. The 2-carboxylic acid does not react. 1-Nitroanthraquinone and conc. HCl at 250–280° give an impure chloroanthraquinone, m.p. 133–135°. 1-Hydroxyanthraquinone-2-sulphonic acid in cold H_2O with excess of Br in KBr (high temp. causes disruption of anthraquinone ring) gives 4-bromo-1-hydroxyanthraquinone-2-sulphonic acid [K salt is converted by aq. $\text{Ba}(\text{OH})_2$ at 200° into a trace of purpurin, or by 80% H_2SO_4 at 170° into 4-bromo-1-hydroxyanthraquinone]. K_2 anthrarufin-2:6-disulphonate and Br in H_2O (cold) give a Br_4 -derivative (K_2 salt). Alizarin-3-sulphonic acid and excess of Br give the 4-Br-derivative (K salt, +2 H_2O). Quinizarin-3-sulphonic acid does not react similarly. 1-Aminoanthraquinone-2-sulphonic acid (from 1% aq. solution of Na salt and HBr) and Br-KBr at 100° afford 2:4-dibromo-1-aminoanthraquinone, m.p. 214°. 4:8-

Diaminoanthrarufin-2:6-disulphonic acid and $\text{Br}\cdot\text{H}_2\text{O}$ give a substance possessing dyeing properties.

A. T. P.

Structure of aniline-black. III. Structure and mechanism of formation of Willstätter's imines. J. S. JOFFE and V. J. SOLOVEITSCHIK (J. Gen. Chem. Russ., 1939, 9, 129—143).—In presence of 0.5 mol. of FeCl_3 per mol. of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$ (I) the sole product is $pp'p''$. $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (II) (*Ac* derivative, m.p. 199—200°), whilst with excess of FeCl_3 the product is $pp'p''$. $\text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ (III). The reactions are represented: (I) $\rightarrow \text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ [(I)] \rightarrow (II) \rightarrow (III). (I) and 4:1:2- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_3\text{H}$ (IV) (12 hr. at 160—170°, in presence of MgCO_3) yield 4-nitro-4'-anilindiphenylamine-2-sulphonic acid, reduced (Zn in NaOH) to the corresponding 4- NH_2 -compound. This is hydrolysed with 10% HCl to 4-amino-4'-anilindiphenylamine (V), m.p. 154°, which condensed with (IV) gives 4-anilino-4'-(4'-nitro-2'-sulphoanilino)diphenylamine, hydrolysed and reduced (as above) to (II). NHPh_2 with $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NO}$ in 80% H_2SO_4 at -5° yields *N*-acetyl-*N'*-*p*-anilino-phenyl-1:4-benzoquinonedi-imine, m.p. 178—180°, reduced by $\text{NHPh}\cdot\text{NH}_2$ to the *Ac* derivative, m.p. 168°, of (V). Similarly, NHPh_2 and 4-nitroso-4'-acetamidodiphenylamine yield the *Ac* derivative, m.p. 179—180°, of (III), reduced by $\text{NHPh}\cdot\text{NH}_2$ to that of (II). R. T.

Reaction of *p*-phenylenediamine and its derivatives with diazonium salts. III. Transformation of diazonium salts. J. S. JOFFE and V. J. SOLOVEITSCHIK (J. Gen. Chem. Russ., 1939, 9, 114—118).—The following reactions take place when diazotised amines are added to $pp'p''$. $\text{NHPh}\cdot[\text{C}_6\text{H}_4\cdot\text{NH}]_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (I): (I) + $2\text{RN}_2\cdot\text{OH} \rightarrow \text{NHPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ (II) + R_2 + $2\text{H}_2\text{O}$ + N_2 ; (II) + $2\text{RN}_2\cdot\text{OH} \rightarrow \text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}$ (III) + R_2 + $2\text{H}_2\text{O}$ + N_2 ; (III) + $\text{RN}_2\cdot\text{OH} \rightarrow \text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}$ + H_2O + N_2 ($\text{R} = o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot, p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot, 2:5\text{-C}_6\text{H}_3\text{Cl}_2$). R. T.

Use of *dl*-menthol for the preparation of biosynthetic glucuronic acid. R. T. WILLIAMS (Nature, 1939, 143, 641; cf. A., 1938, III, 1041).—*dl*-Menthol conjugates with glucuronic acid to the extent of 60% in the rabbit, and affords the best method of obtaining relatively large amounts of this acid, which can then be readily isolated as the NH_4 salt. This contains ~60% of *d*- and 40% of *l*-acid, and can be resolved by fractional crystallisation from H_2O . *d*-Menthyl- β -*d*-glucuronide, m.p. 110—112°, $[\alpha]_D^{25} +5^\circ$ in alcohol, is thus obtained. L. S. T.

Ethinylborneol.—See B., 1939, 578.

Sesquiterpenes. XLIII. Constitution of the caryophyllene mixture. Degradation of dihydrocaryophyllene. L. RUZICKA, K. HUBER, P. A. PLATTNER, S. S. DESHPANDE, and S. STUDER (Helv. Chim. Acta, 1939, 22, 716—727).—Technical caryophyllene (I), b.p. 118—121°/10 mm., $\alpha_D -7.4^\circ$ to -8.8° ($l = 1$), is hydrogenated (Raney Ni in MeOH) to dihydrocaryophyllene, b.p. 122—123°/12 mm., α_D

-14° ($l = 1$), which is converted by successive treatments with O_3 in AcOH and warm H_2O into a non-cryst. *Me* ketocarboxylate, $\text{C}_{16}\text{H}_{28}\text{O}_3$, b.p. 117—120°/~1 mm., $\alpha_D +47^\circ$ ($l = 1$), and non-investigated neutral products. The corresponding acid is transformed by NaOH and Br into CHBr_3 and a non-cryst. dicarboxylic acid, $\text{C}_{14}\text{H}_{24}\text{O}_4$, converted by CH_2N_2 into the *Me*₂ ester, b.p. 106—108°/~1 mm., $\alpha_D +39^\circ$ ($l = 1$) (corresponding dianilide, m.p. 188°). The Th salt of the acid passes at ~370° into a mixture of ketones, $\text{C}_{13}\text{H}_{22}\text{O}$, (A) b.p. 62—63°/~1 mm., $\alpha_D +44^\circ$ ($l = 1$) (semicarbazone, m.p. 188—190°), which gives a pale yellow colour with $\text{C}(\text{NO}_2)_4$ and very slowly absorbs O from $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in Et_2O at 0° , and (B), b.p. 62—65°/~1 mm., $\alpha_D -42^\circ$ ($l = 1$) (semicarbazone, m.p. 145°), which gives a pale yellow colour with $\text{C}(\text{NO}_2)_4$ and appears to contain $\alpha\beta$ -unsaturated components. A is transformed by HCO_2Et and NaOMe in Et_2O into the non-cryst. $\text{OH}\cdot\text{CH}_2$ derivative, ozonised to the acid, $\text{C}_{13}\text{H}_{22}\text{O}_4$, (*Me*₂ ester, b.p. ~155°/10 mm.), the Th salt of which passes into the ketone, $\text{C}_{12}\text{H}_{20}\text{O}$, isolated as the semicarbazone, m.p. 153.5—156.5°, which is hydrogenated to the compound, $\text{C}_{13}\text{H}_{25}\text{ON}_3$, m.p. 113—114°. The yields in the series are not good but the sequence establishes the great probability that at least one component of (I) has a 7-membered ring (Rydon, A., 1938, II, 107). Homocaryophyllenic acid is cyclised through the Th salt to a ketone, the semicarbazone, m.p. 184—185°, of which is hydrogenated (PtO_2 in AcOH at room temp.) to the semicarbazido-compound, $\text{C}_{10}\text{H}_{19}\text{ON}_3$, m.p. 172—174°. SeO_2 oxidises (I) in Ac_2O to a mixture of dihydrocaryophyllenols, b.p. 155—158°, which could not be caused to react with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ in $\text{C}_6\text{H}_5\text{N}$; it is oxidised by CrO_3 in AcOH mainly to neutral products from which a semicarbazone, $\text{C}_{16}\text{H}_{27}\text{ON}_3$, m.p. 243°, $[\alpha]_D +68.8^\circ$, is isolated. The absorption spectrum corresponds with that of an $\alpha\beta$ -unsaturated aldehyde or ketone. H. W.

Terpenochromogenic or terpenochromic compounds. II. Spectroscopic examination of the pigments formed in the EM reaction with essential oils. A. MÜLLER (J. pr. Chem., 1939, [ii], 153, 77—90).—Examination of the common absorption bands of the terpenochromes formed from a large no. of essential oils (apart from those which show continuous absorption in the region 400—490 $\text{m}\mu$.) permits the discrimination of two main types of terpenochromogenic components with the approx. structure of bisabolene and the azulogen type. The former, which are rather widely distributed in essential oils, form with the EM reagent pigments which absorb mainly in the region 480—530 $\text{m}\mu$. The latter show more bands in the region 530—700 $\text{m}\mu$. which are closely similar to the visible absorption bands of the true azulenes. H. W.

Marrubiin, a diterpenoid lactone. (Miss) F. HOLLIS, J. H. RICHARDS, and A. ROBERTSON (Nature, 1939, 143, 604; cf. A., 1908, i, 344).—Marrubiin (I), m.p. 158°, $\text{C}_{20}\text{H}_{32}\text{O}_5$, gives on hydrolysis a monobasic acid (II), $\text{C}_{20}\text{H}_{30}\text{O}_5$, m.p. 197° (*Me*, m.p. 85°, and *Et* ester, m.p. 88°). Hydrogenation of (I) and (II) gives the corresponding H_4 -derivatives, m.p. 132°

and 187° (*Et* ester, m.p. 95°), respectively. (I) contains 1 OH, which is probably a *tert.*-OH; the fourth O is present in an oxide system. (I) is readily resinified by warm mineral acids and by hot HCO_2H , and is oxidised (KMnO_4) to a neutral compound, m.p. 211°, and a lactone, m.p. 161° (acid, m.p. 208°), which, with a liquid acid, is also formed by the action of O_3 . Dehydrogenation (Se) yields 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$ (agathaline). (I) is a hydroxyditerpene lactone of the manoyl oxide type. L. S. T.

Lupeol. IV. F. BIEDEBACH (Arch. Pharm., 1939, 277, 163—173; cf. A., 1938, II, 288).—Oxidation (CrO_3) of lupeol acetate yields a keto-acetate (I), $\text{C}_{31}\text{H}_{50}\text{O}_3$, m.p. 265° (Heilbron *et al.*, A., 1938, II, 195, give $\text{C}_{32}\text{H}_{52}\text{O}_3$), a neutral substance, $\text{C}_{32}\text{H}_{52}\text{O}_3$, m.p. 259°, and a mixture of acids, the Na salts of which on methylation and further oxidation yield Me ketolupanecarboxylates, (II), m.p. 263°, and (III), m.p. 201° [2:4-dinitrophenylhydrazones, m.p. 157° (sintering at 135°)], hydrolysed to the acids, m.p. 266° and 281° respectively. Hydrolysis of (I) yields the keto-alcohol, $\text{C}_{29}\text{H}_{48}\text{O}_2$, oxidised (CrO_3) to a diketone (IV), $\text{C}_{29}\text{H}_{46}\text{O}_2$, m.p. 208°. Oxidation (CrO_3) of lupeol gives the above keto-acids, and (IV). Reduction (Clemmensen) followed by methylation of (II) and (III) affords the *Me lupanecarboxylates*, m.p. 225—228° and 194—197° respectively. Lupeol with K in $\text{C}_5\text{H}_{11}\cdot\text{OH}$ -PhMe, followed by CS_2 and then MeI, yields *Me lupeylxanthogenate*, m.p. 207°. Thermal decomp. of this or of lupeol benzoate yields the same lupylene. *Lupeol acetate dibromide*, m.p. 225° (from lupeol acetate and Br in $\text{CHCl}_3\text{-AcOH}$), with AgNO_3 in $\text{C}_5\text{H}_5\text{N}$ gives *bromolupeol acetate*, m.p. 205° (sintering at 197°). Bromolupeol is unaffected by boiling EtOH-KOH . A. LI.

Triterpenes. XLVI. Keto-derivatives and oxides of the α - and β -amyrin series. L. RUZICKA, G. MÜLLER, and H. SCHELLENBERG (Helv. Chim. Acta, 1939, 22, 758—766).—Oxidation of β -amyrin acetate (I) by CrO_3 in AcOH affords *keto- β -amyrin acetate*, m.p. 264—265°, whilst β -amyrin benzoate similarly affords *keto- β -amyrin benzoate*, m.p. 262—263°, $[\alpha]_D + 154.5^\circ$ in CHCl_3 , either of which is hydrolysed by alkali to *keto- β -amyrin*, m.p. 230—231°, $[\alpha]_D + 102^\circ$ in CHCl_3 , converted by the more protracted action of alkali into a compound, $\text{C}_{30}\text{H}_{48}\text{O}_2$, m.p. 247—248°, $[\alpha]_D + 81.5^\circ$ in CHCl_3 . The difference between these observations and those of Beynon *et al.* (A., 1938, II, 416) is unexplained. The compound obtained from (I) and H_2O_2 , m.p. 292—293°, has in CHCl_3 an absorption max. at 2900 Å. and the “ β -amyrin oxide” obtained therefrom by alkaline hydrolysis has m.p. 207—208°, absorption max. 2800 Å.; it is therefore ketodihydro- β -amyrin, identical with the compound derived from β -amyrin and BzO_2H . The absorption curves of β -amyrilene dioxide and β -hydroamyrlene oxide have max. at ~2800—2900 Å. The spectra of α -amyrlene oxide, m.p. 173° and 133°, and of α -cholestene oxide are recorded. The results show that in the amyirin series oxido-groups are stable only in ring A whereas in ring C they pass into CO groups. Improved directions for the oxidation of α -amyrin to α -amyrene (II), m.p. 125—126°, are given; the semicarbazone,

m.p. 204—205°, is best obtained by triturating $\text{NH}_2\text{CO-NH-NH}_2\cdot\text{HCl}$ with cryst. NaOAc and MeOH , filtering, and adding the filtrate to (II) in $\text{Et}_2\text{O-MeOH}$ at room temp. This is converted by NaOEt in EtOH at 180° into α -amyrene, m.p. 124°, $[\alpha]_D + 95^\circ$ in CHCl_3 . All m.p. are corr. H. W.

Triterpenes. XLVII. Introduction of new double linkings in the α - and β -series. L. RUZICKA, G. MÜLLER, and H. SCHELLENBERG (Helv. Chim. Acta, 1939, 22, 767—777).—Protracted heating of keto- β -amyrin with a large excess of MgMeI gives a jelly, which is acetylated to *methyldehydro- β -amyrin acetate*, $\text{C}_{33}\text{H}_{52}\text{O}_2$, m.p. 225—226°, $[\alpha]_D + 133^\circ$ in CHCl_3 , which shows an absorption band at 2400 Å. characteristic of a conjugated double linking. Under similar conditions keto- α -amyrin yields *methyldehydro- α -amyrin*, m.p. 148—152°, which gives an acetate, m.p. 228—230°, $[\alpha]_D + 144^\circ$ in CHCl_3 , obtained also from keto- α -amyrin acetate and MgMeI . β -Amyrin acetate (I) is readily oxidised by SeO_2 in boiling AcOH to a *dehydro- β -amyrin acetate*, m.p. 228—229°, $[\alpha]_D - 62^\circ$ in CHCl_3 , hydrolysed by alkali to *dehydro- β -amyrin*, m.p. 228—229°, $[\alpha]_D - 72^\circ$ in CHCl_3 , which could not be hydrogenated (PtO_2 in dioxan) and does not add maleic anhydride; it appears to have a conjugated double linking. It is also obtained by hydrolysis of *dehydro- β -amyrin benzoate*, m.p. 249—250°, $[\alpha]_D - 34^\circ$ in CHCl_3 . β -Amyrene under similar conditions affords *dehydro- β -amyrene*, m.p. 218—219°, $[\alpha]_D - 73^\circ$ in CHCl_3 . The corresponding α -acetate and -benzoate are unchanged by protracted boiling with SeO_2 . β -Amyrin benzoate and S at 230—240° give (after hydrolysis) a compound, $\text{C}_{30}\text{H}_{44}\text{OS}$, m.p. 201°, whilst (I) yields a substance, $\text{C}_{32}\text{H}_{46}\text{O}_2\text{S}$, m.p. 199—200°; the crude oxidation product when cryst. repeatedly from $\text{MeOH-H}_2\text{O}$ give small amounts of an unidentified material, m.p. 251°, and a ketone, $\text{C}_{30}\text{H}_{44}\text{O}_3$, m.p. 281—282° (acetate, m.p. 231—232°, oxidised to an *acetyl-lactone*, $\text{C}_{32}\text{H}_{44}\text{O}_5$, m.p. 278—279°). Keto- α -amyrin is converted by Na and amyl alcohol into a substance, $\text{C}_{35}\text{H}_{60}\text{O}_3$, m.p. 225—226°, $[\alpha]_D - 50.5^\circ$ in CHCl_3 , which gives only a faint colour with $\text{C}(\text{NO}_2)_4$. Under these conditions α -amyrin is unchanged. All m.p. are corr. H. W.

Triterpenes. XLVIII. Products of the oxidation of lupeol and esters of lupeol with monoperphthalic acid and with selenium dioxide. L. RUZICKA and G. ROSENKRANZ (Helv. Chim. Acta, 1939, 22, 778—788).—In agreement with Heilbron *et al.* (A., 1938, II, 195) and contrary to Dieterle *et al.* (*ibid.*, 288), lupeol absorbs only one mol. of O_2 from $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in 24 or 120 hr. giving *lupeol oxide* (I), m.p. 192—197°, $[\alpha]_D + 8.83^\circ$ in CHCl_3 , whilst dihydrolupeol is unaffected. *Lupeol acetate oxide* (II), m.p. 226—230° after softening at 218—222°, $[\alpha]_D + 24^\circ$ in CHCl_3 , obtained by oxidation of the acetate, is hydrolysed by alkali to a mixture of approx. equal parts of (I) and the aldehyde, *lupanolol* (III), $\text{C}_{30}\text{H}_{50}\text{O}_2$, m.p. 173—175°, $[\alpha]_D + 8.9^\circ$ in CHCl_3 , and is converted almost quantitatively by acid into (III) (*oxime*, m.p. 221—222°; *acetate*, m.p. 223—226°, $[\alpha]_D + 14.4^\circ$ in CHCl_3). Oxidation of (III) by CrO_3 gives *acetylisolupanollic acid*, m.p. 290—291° (vac.), $[\alpha]_D + 24.3^\circ$ in CHCl_3 [*Me* ester, m.p. 280—281° (vac.)],

$[\alpha]_D + 0.4^\circ$ in CHCl_3 , hydrolysed by protracted boiling with $2N$ -KOH-EtOH to the OH-acid, m.p. $290-291^\circ$, $[\alpha]_D + 8.44^\circ$ in CHCl_3 , and a neutral substance, $\text{C}_{31}\text{H}_{50}\text{O}_3$ or $\text{C}_{32}\text{H}_{52}\text{O}_3$, m.p. $267-268^\circ$, $[\alpha]_D + 0.80^\circ$ in CHCl_3 . Lupeol acetate (IV) is oxidised by SeO_2 in boiling Ac_2O to *lupenediol diacetate*, m.p. $178-179^\circ$, which gives a pale yellow colour with $\text{C}(\text{NO}_2)_4$ and is hydrolysed to *lupenediol*, m.p. $227.5-228.5^\circ$. Lupeol benzoate is transformed by SeO_2 in boiling C_6H_6 into *ketolupeol benzoate*, $\text{C}_{37}\text{H}_{52}\text{O}_3$, m.p. 268.5° , which does not contain an active H, does not give a yellow colour with $\text{C}(\text{NO}_2)_4$, but gives an *oxime*, m.p. $235-237^\circ$. It is hydrolysed to *ketolupeol*, m.p. $232-233^\circ$. Under similar conditions, (IV) gives a substance, $\text{C}_{32}\text{H}_{48(50)}\text{O}_3$, m.p. $224-226^\circ$. H. W.

Triterpenes. XLIX. Oxidation of methyl acetyloleanolate and methyl acetylsumaresinonate with selenium dioxide. L. RUZICKA, A. GROB, and F. C. VAN DER SLUYS-VEER (Helv. Chim. Acta, 1939, 22, 788-792).—Oxidation of Me acetyloleanolate with SeO_2 in boiling AcOH gives a strongly unsaturated substance, (?) $\text{C}_{33}\text{H}_{46}\text{O}_6$, m.p. $245-246^\circ$, $[\alpha]_D + 146^\circ$ in CHCl_3 , and Me acetyldihydro-oleanolate, $\text{C}_{33}\text{H}_{50}\text{O}_4$, m.p. $227-228^\circ$, $[\alpha]_D + 137^\circ$ in CHCl_3 , which contains two conjugated double linkings, probably in the same ring. Alkaline hydrolysis converts it into Me *dehydro-oleanolate*, m.p. $168-169^\circ$. Similarly, Me acetylsumaresinonate is oxidised to Me *dehydro-acetylsumaresinonate*, m.p. $302-303^\circ$, $[\alpha]_D - 151.6^\circ$ in CHCl_3 , the absorption spectrum of which indicates the presence of CO and two conjugated double linkings. H. W.

Triterpene group. V. Oxidation products of the β -amyrin derivative, $\text{C}_{30}\text{H}_{44}\text{OS}$. J. C. E. SIMPSON (J.C.S., 1939, 755-759).—Oxidation (CrO_3 -AcOH) of the OH-ketone (I), $\text{C}_{30}\text{H}_{44}\text{O}_3$, obtained from the keto-acetate oxidation product (improved prep.) of the compound, $\text{C}_{30}\text{H}_{44}\text{OS}$ (improved prep., cf. Jacobs *et al.*, A., 1930, 1292), gives a *diketone*, $\text{C}_{30}\text{H}_{42}\text{O}_3$, m.p. $289-290^\circ$, $[\alpha]_D^{18} - 94^\circ$ [*monosemicarbazone*, m.p. $287-289^\circ$ (decomp.)], which with HNO_3 affords a NO_2 -compound, $\text{C}_{30}\text{H}_{42}\text{O}_7\text{N}_2$, m.p. $219-220^\circ$ (decomp.), $[\alpha]_D^{18} - 87^\circ$, also obtained from (I) and HNO_3 . The hydroxy-keto-lactone (II), $\text{C}_{30}\text{H}_{42}\text{O}_4$ (oxidation product of $\text{C}_{30}\text{H}_{44}\text{OS}$), is oxidised (CrO_3 -AcOH) to a *diketo-lactone*, $\text{C}_{30}\text{H}_{40}\text{O}_4$, m.p. $250.5-252^\circ$, $[\alpha]_D^{18} + 66^\circ$ (*monoxime*, m.p. $307-310^\circ$), which with HNO_3 yields a NO_2 -compound, $\text{C}_{30}\text{H}_{42}\text{O}_7\text{N}_2$, m.p. $223.5-224.5^\circ$ (decomp.), $[\alpha]_D^{18} + 49^\circ$, also derived from (II) and HNO_3 . The structural relationship between the NO_2 -compounds is the same as between (I) and (II). Oxidation of (II) with CrO_3 - H_2SO_4 gives (small yield) a *lactone*, $\text{C}_{28}\text{H}_{38}\text{O}_4$, m.p. $259-260^\circ$, $[\alpha]_D^{14} - 271^\circ$, and an acid, isolated as the Me ester, $\text{C}_{32}\text{H}_{44}\text{O}_7$, m.p. $216.5-217.5^\circ$, $[\alpha]_D^{18} - 31.7^\circ$; the lactone is hydrolysed (KOH) to an acid, isolated as the Me ester, $\text{C}_{29}\text{H}_{42}\text{O}_5$, m.p. $210-211^\circ$. The acetate of (I) is oxidised (CrO_3 - H_2SO_4) to an *acetate*, $\text{C}_{32}\text{H}_{44}\text{O}_8$, m.p. $342-344^\circ$ (decomp.), $[\alpha]_D^{18} + 63^\circ$, hydrolysed (KOH) to an *alcohol*, $\text{C}_{30}\text{H}_{42}\text{O}_5$, m.p. $337-339^\circ$, $[\alpha]_D^{18} + 26.7^\circ$. These data are difficult to explain on the structure for β -amyrin suggested by Ruzicka *et al.* (A., 1937, II, 202). (All rotations measured in CHCl_3 .) F. R. S.

Hydrocarbon $\text{C}_{20}\text{H}_{28}$.—See B., 1939, 582.

Volatile plant substances. X. Vetivones, the odoriferous constituents of oil of vetiver. A. S. PFAU and P. A. PLATTNER (Helv. Chim. Acta, 1939, 22, 640-654; cf. A., 1939, II, 148).—The attempted isolation of the ketones from the oil by means of $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ gives a large proportion of resins. Girard's reagent P can be applied directly to the oil but the regeneration of the ketones is difficult. With $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ an enriched fraction of the oil gives β -*vetivonesemicarbazone* (I), m.p. $228-229^\circ$, $[\alpha]_D^{20} - 71^\circ$ in AcOH, and α -*vetivonesemicarbazone*, m.p. $210-212^\circ$ (decomp.), $[\alpha]_D^{20} + 316^\circ$ in AcOH. These are hydrolysed by $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ to β - (II), b.p. $153-154^\circ/4$ mm., m.p. $44-44.5^\circ$, $[\alpha]_D^{20} - 24.1^\circ$ in EtOH, and α -, b.p. $152-153^\circ/4$ mm., $[\alpha]_D^{20} + 225^\circ$ in EtOH, *vetivone*. (II) does not appear to combine with NaHSO_3 . (I) is transformed by conc. aq. KOH containing CuSO_4 into the *hydrocarbon*, $\text{C}_{15}\text{H}_{24}$, b.p. $110-112^\circ/2.5$ mm., which does not give a cryst. hydrochloride. $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH at room temp. transforms (II) into a *hydrocarbon*, $\text{C}_{15}\text{H}_{22}$, b.p. $110^\circ/3.6$ mm., and β -*vetivol*, b.p. $129-132^\circ/0.5$ mm. (II) is reduced by Na and EtOH or catalytically (Ni-95% EtOH at 70°) to β -*dihydrovetivol* (III), b.p. $144^\circ/2.4$ mm., m.p. 107° (3 : 5-dinitrobenzoate, dimorphous, m.p. 121° or $129.5-130^\circ$). β -Dihydrovetivone, obtained during the partial hydrogenation of (II), is characterised by a *dibenzylidene* derivative, m.p. $130.5-131.5^\circ$. Hydrogenation (PtO_2 in AcOH) of (II) or (III) leads to β -*tetrahydrovetivol*, m.p. $76-76.5^\circ$, oxidised to β -*tetrahydrovetivone*, b.p. $139^\circ/3$ mm., m.p. $37.5-38^\circ$ (*dibenzylidene* derivative, m.p. $101.5-102^\circ$). The mixture of dextrorotatory semicarbazones obtained during the isolation of (I) gives *isovetivones*, reduced (Na-EtOH) to *dihydroisovetivols*, b.p. $153^\circ/4$ mm. H. W.

Action of nitric acid on wood. Chemistry of lignin. R. S. HILPERT, W. KRÜGER, and G. HECHLER (Ber., 1939, 72, [B], 1075-1082).—The action of HNO_3 (d 1.51) on red beech or pine wood resembles that on cotton wool or sulphite cellulose but the nitrated wood is only partly sol. in 72% H_2SO_4 , in which the nitrated cellulose (I) dissolves completely, and is almost completely denitrated by $(\text{NH}_4)_2\text{S}$, which reduces the N content of (I) to $\sim 2\%$ only. The solution obtained by nitrating wood when diluted with H_2O gives a yellow ppt. (II) which according to analysis is not aromatic and may consist of 5 ($\text{C}_6\text{H}_{10}\text{O}_5 - \text{H}_2\text{O}$) units into which 7 NO_2 residues have entered. The bulk of the N is present as NO_3 . The ppt. gives NH_3 when warmed with alkalis and HCN when treated with acids. Methylated beechwood is almost completely sol. in HNO_3 and is very largely pptd. from the solution by H_2O ; the N content is \ll that of the product from wood. Evaporation to dryness of the filtrate from (II) leaves a dark yellow powder (III) in which \sim half the N is present as NO_3 and the other half in another form, chiefly as NH_3 and HCN. Sucrose, when treated successively with HCl and HNO_3 , gives a solution which, when evaporated to dryness, leaves a residue similar to (III). Pine lignin (15% OMe) behaves towards conc. HNO_3 very similarly to methylated

sucrose lignin, supporting the authors' view that the lignins are products of the action of conc. acids on cellulose. The reaction between wood and dil. HNO_3 can be regarded fundamentally as a hydrolysis followed by further change of the products by acid. In explanation of the formation of HCN it is shown that aromatic compounds react rapidly with dil. HNO_3 only if free OH is present. With $\text{o-OH-C}_6\text{H}_4\text{-CO}_2\text{H}$, PhOH , and vanillin the change occurs rapidly at 100° with immediate formation of HCN, whereas piperonal and methylated vanillin react much more slowly. Furfuraldehyde is first resinified and then nitrated with evolution of HCN. Further arguments are adduced against the aromatic character of lignin. H. W.

Lignin. K. FREUDENBERG (Angew. Chem., 1939, 52, 362—363).—Of every 100 phenylpropane groups (I) in pine lignin, ~70 belong to the guaiacyl, 25 to the piperonyl, and 5 to the syringyl type. At most 18% of the side-chains are of the type OH-CHAc and -CO-CHMe-OH . Only a small proportion, if any, of (I) are present in unimol. form, probably as glucosides. Most are combined among themselves. Most of the reactions of lignin are best interpreted on the assumption that the side-chain is $\text{-CH(OH)-CH(OH)-CH}_2\text{-OH}$, -CHAc-OH , or $\text{-CH(OH)-CH}_2\text{-CHO}$. In wood and in isolated lignin the p -OH groups are substituted but do not participate in glucoside formation. Pine lignin appears to contain ether linkings and all its characteristic reactions can be regarded from the single viewpoint of ether scissions. The most important observations bearing on its constitution are the isolation of veratric and isohemipinic acid after methylation and oxidation, the prep. from it of vanillin by oxidation in such a manner that the scaffold is degraded while the product remains intact, and the identification of the substance 4:3:1- $\text{OHC}_6\text{H}_3(\text{OMe})\text{-CO-CHMe-OH}$ as product of the action of HCl-EtOH on pine wood. Since beech lignin gives notably more AcOH than pine lignin when oxidised with CrO_3 it contains more terminal Me groups. The greater instability of deciduous tree lignin (II) towards degrading agents such as HCl-EtOH is due to the syringyl component which is capable of ether formation but not of further condensation. It is therefore obvious that simpler degradation products in better yield are obtained from (II) than from pine lignin. H. W.

Lignin and methylated hydrocarbons extracted from fir-wood by dioxan. III. I. M. ORLOVA and N. I. NIKITIN (J. Appl. Chem. Russ., 1939, 12, 76—84).—The $\text{H}_2\text{O-insol.}$ fraction of the lignin extracted by dioxan from the wood (at 90°) is treated according to Freudenberg (A., 1936, 995), to yield 9.4—12.2% of veratric acid. The ultra-violet absorption spectrum of the fraction in question closely resembles that of ordinary lignin and of isoeugenol. The $\text{H}_2\text{O-sol.}$ fraction contains OH- 22—25 and OMe-groups 7%, and appears to consist of low mol. wt. polysaccharides, containing methylated sugars. R. T.

Study of larch lignin by the method of alkaline fusion. T. I. RUDNEVA and N. I. NIKITIN (J. Appl. Chem. Russ., 1939, 12, 72—75).—Treatment of larch lignin by the method of Freudenberg *et al.* (A., 1936,

995) gives 11.3% of veratric acid. Veratroylformic acid was also detected. The lignin thus contains pyrocatechol groups. R. T.

Shellac. XII. Degradations of shellolic acid. W. NAGEL and W. MERTENS (Ber., 1939, 72, [B], 985—992; cf. A., 1938, II, 24).—Treatment of shellolic acid (I) with CPh_3Cl gives only non-cryst. products. The action of Br on (I) (*loc. cit.*) is now regarded as simple substitution and lactonisation with production of the Br-lactonic acid, $\text{C}_{15}\text{H}_{17}\text{O}_5\text{Br}$ (II), which is converted by aq. K_2CO_3 at 100° into the dicarboxylic acid, $\text{C}_{15}\text{H}_{18}\text{O}_6$. The free OH in (II) is so resistant that the action of PBr_5 gives a bromide, which is transformed into the amide, $\text{C}_{15}\text{H}_{19}\text{O}_5\text{N}$, m.p. 256° , in which it is still intact (Zerevitinov). CH_2N_2 transforms (I) into a mixture of the Me_1 ester, m.p. $169\text{—}170^\circ$, and the Me_2 ester, m.p. 180° (formed by opening of the lactone ring). Attempts to obtain either exclusively were fruitless so that the production of an equilibrium is assumed. The mixture could not be caused to react with AcCl or $\text{PhSO}_2\text{Cl} + \text{C}_5\text{H}_5\text{N}$. Zn dust and boiling dil. HCl transform (I) into deoxyshellolic acid, $\text{C}_{15}\text{H}_{18}\text{O}_5$ (Me_2 ester, m.p. 68°). Me_2 shellolate and MgPhBr in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ at 60° yield apparently a Ph_4 derivative, $\text{C}_{39}\text{H}_{40}\text{O}_4$, m.p. indef., which is stable towards KMnO_4 and contains only 2 OH, indicating that an ether ring has probably been formed. Oxidation of (I) with KMnO_4 in alkaline solution gives the dilactone, $\text{C}_{15}\text{H}_{18}\text{O}_6\text{-H}_2\text{O}$, m.p. 162° after loss of H_2O at 124° (Ac derivative, m.p. 246°); this is oxidised by KMnO_4 ($=4\text{ O}$) in neutral solution to the monocarboxylic acid, $\text{C}_{14}\text{H}_{16}\text{O}_6$, m.p. 248° , which contains 2 OH (Zerevitinov) and gives a Me ester, m.p. 154° . In faintly acid solution (I) is oxidised by KMnO_4 at 20° to the acid, $\text{C}_{13}\text{H}_{16}\text{O}_6\text{-2H}_2\text{O}$, m.p. $153\text{—}155^\circ$ after loss of H_2O at $80\text{—}90^\circ$ (Me ester, m.p. $79\text{—}80^\circ$). H. W.

Sapogenins. III. Dehydrogenation products of methylsarsasapogenin and methylcholestanol. G. A. R. KON and A. M. WOOLMAN. IV. Sapogenin of *Balanites aegyptica*, Wall. G. A. R. KON and W. T. WELLER (J.C.S., 1939, 794—800, 800—801).—III. *o*-Bromobenzylmalonic acid, m.p. 149° (decomp.), prepared from *o*- $\text{C}_6\text{H}_4\text{Br-CH}_2\text{Cl}$ and $\text{CHNa}(\text{CO}_2\text{Et})_2$, is decarboxylated to β -*o*-bromophenylpropionic acid, which through the chloride gives AlCl_3 4-bromohydrindone, reduced (Zn-HCl) to the hydrindene; the Grignard reagent from this compound does not react with $(\text{CH}_2)_2\text{O}$. Bromination of 7:1- $\text{C}_{10}\text{H}_6\text{Me-O-Me}$ gives 1-bromo-4-methoxy-6-methylnaphthalene, m.p. 72° [Br_2 -compound (1:5 ?), m.p. 72°], which through the Grignard compound and $(\text{CH}_2)_2\text{O}$ affords β -4-methoxy-6-methyl-1-naphthylethyl alcohol, m.p. 73° ; the bromide of the alcohol does not condense satisfactorily with 2:5-dimethylcyclopentanone. cyclo-Hexenylacetyl chloride and 1- $\text{C}_{10}\text{H}_7\text{-MgBr}$ yield Δ^1 -cyclohexenyl-1-acetonaphthone, reduced and cyclised (P_2O_5) to 1:2:3:4:11:12:13:14-octahydrochrysene [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ complex, m.p. $147\text{—}148^\circ$]. 2-Methylcyclopentanone, $\text{CH}_2\text{Br-CO}_2\text{Me}$, and Mg give a OH-ester, dehydrated and hydrolysed to 2-methyl- $\Delta^{1(2)}$ -cyclopentenylacetic acid, m.p. 50° , the chloride of which can not be condensed with 1-bromo-4-methoxy-6-methylnaphthalene. 2-Methyl-6-aceto-

naphthone and furfuraldehyde yield *furfurylidene-2-methyl-6-acetonaphthone*, m.p. 121°, hydrolysed to δ^1 -diketo- η -(6-methyl-2-naphthyl)heptonic acid, m.p. 181°, which with KOH affords 3-(6'-methyl-2'-naphthyl)- Δ^2 -cyclopenten-1-one-2-acetic acid, m.p. 188°. This and Ac_2O give 3'-keto-4-acetoxy-7-methyl-1:2-cyclopentenophenanthrene (I), m.p. 224° (decomp.) [hydroxy-ketone, m.p. 290° (decomp.)], which is hydrogenated under drastic conditions and then dehydrogenated (Pd-C) to 7-methyl-1:2-cyclopentenophenanthrene, m.p. 132° [styphnate, m.p. 182—183°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ complex, m.p. 183—183.5°], identical with one of the dehydrogenation products of methylsarsapogenin and of methylcholestanol (II). Hydrolysis and methylation (Me_2SO_4) of (I) gives 3'-keto-4-methoxy-7-methyl-1:2-cyclopentenophenanthrene, m.p. 190—191°, which with MgMeI affords 4-methoxy-3':7-dimethyl-1:2-cyclopentenophenanthrene, m.p. 130—131°. This is hydrogenated at room temp. to 4-methoxy-3':7-dimethyl-, m.p. 83—84° [$s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 184—185°], and under drastic conditions to 3':7-dimethyl-1:2-cyclopentenophenanthrene, m.p. 139—140° [picrate, m.p. 128°; styphnate, m.p. 161°; $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 154—155°], identical with one of the dehydrogenation compounds from (II). Dehydrogenation of 3-methylcholestanol affords the two hydrocarbons and a third hydrocarbon, $\text{C}_{28}\text{H}_{46}$, m.p. 207—208° (derivative with 2:7-dinitroanthraquinone, m.p. 235°), which is a homologue of Diels' hydrocarbon (absorption spectrum). These results confirm the position previously assigned to the OH of sarsapogenin (cf. Farmer *et al.*, A., 1937, II, 203); they also show that in the dehydrogenation of sterol-like compounds the migration of the angular Me from C_{13} to C_{17} is not invariably the rule and that complete elimination of this group can sometimes occur.

IV. A sapogenin, *nitogenin*, $\text{C}_{27}\text{H}_{44}\text{O}_3$, m.p. 201°, $[\alpha]_D -112^\circ$ in CHCl_3 (*Ac*, m.p. 191—192°, and *Bz* derivatives, m.p. 229°), has been isolated from the saponin occurring in the seed kernels. It is very closely related to tigogenin. F. R. S.

Saponins and sapogenins. IX. Oxidation of echinocystic acid and derivatives. W. R. WHITE and C. R. NOLLER (J. Amer. Chem. Soc., 1939, 61, 983—989; cf. A., 1938, II, 448).—Echinocystic acid (I) is shown to contain $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{H}$ and a second OH not far removed. Its Me ester (II) is converted by $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4\text{-AcOH-H}_2\text{O}$ at room temp. into an unsaturated $[\text{C}(\text{NO}_2)_2]$ diketo-ester (III), $\text{C}_{28}\text{H}_{43}\text{O}_2\cdot\text{CO}_2\text{Me}$, dimorphic forms, m.p. 166—168° and 192—194°, $[\alpha]_D^{25} +1.6^\circ$, $[\alpha]_{441}^{25} -1.6^\circ$ in dioxan, distils unchanged at 2.5 mm. [oxime, sinters at 254°, m.p. 257.5—259.5° or 260—263°, $[\alpha]_D^{25} -50.0^\circ$, $[\alpha]_{441}^{25} -61.8^\circ$ in dioxan; phenylhydrazone, m.p. 179.5° (decomp.), $[\alpha]_D^{25} -60.4^\circ$, $[\alpha]_{441}^{25} -97.7^\circ$ in dioxan], which resists hydrogenation (Pt), does not condense with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ or PhCHO , contains no active CH_2 or enolic OH, but shows 1 active H. No rearrangement has occurred, as (II) is converted by $\text{H}_2\text{SO}_4\text{-AcOH-H}_2\text{O}$ merely into a monoacetate (IV), dimorphic, m.p. 205—208° and 170—171° (unstable), $[\alpha]_D^{25} +27^\circ$, $[\alpha]_{441}^{25} +32.8^\circ$ in dioxan, which is also obtained by hot AcOH-NaOAc . Hot KOH-EtOH

hydrolyses (III) and decomposes the resulting $\beta\text{-CO-acid}$, yielding *norechinocystenedione* (V), m.p. 210—212°, $[\alpha]_D^{25} -92.7^\circ$, $[\alpha]_{441}^{25} -115.3^\circ$ in dioxan. Zn-Hg in HCl-EtOH reduces (III) to a monoketo-ester, $\text{C}_{31}\text{H}_{48}\text{O}_3$, m.p. 209—212°, $[\alpha]_D^{25} -10.3^\circ$, $[\alpha]_{441}^{25} -15.0^\circ$ in dioxan (no oxime or Ac derivative), from which KOH-EtOH gives *norechinocystenone*, $\text{C}_{29}\text{H}_{46}\text{O}$, m.p. 230—233°, by hydrolysis and loss of CO_2 . CrO_3 in AcOH at room temp. oxidises (IV) to an acetoxy-keto-ester, $\text{C}_{33}\text{H}_{50}\text{O}_5$, dimorphic, m.p. 231—234° or 203—205°, $[\alpha]_D^{25} -9.8^\circ$, $[\alpha]_{441}^{25} -17.7^\circ$ in dioxan, hydrolysed by KOH-EtOH to *norechinocystenolone* (VI), $\text{C}_{29}\text{H}_{46}\text{O}_2$, dimorphic, m.p. 230—233° and 268—271°, $[\alpha]_D^{25} -86.7^\circ$, $[\alpha]_{441}^{25} -106.0^\circ$ in dioxan, which is oxidised by $\text{CrO}_3\text{-AcOH}$ to (V). $\text{Na}_2\text{Cr}_2\text{O}_7$ -oxidation of (I) involves a rearrangement, for it yields *isomerechinocystenedione* [not (V)], m.p. 230—233°, $[\alpha]_D^{25} +85.6^\circ$, $[\alpha]_{441}^{25} +103.2^\circ$ in dioxan, the *Ac* derivative [for prep. cf. (IV)], m.p. 204—207°, $[\alpha]_D^{25} -55.9^\circ$, $[\alpha]_{441}^{25} -65.1^\circ$ in dioxan, of which is converted by $\text{H}_2\text{SO}_4\text{-MeOH}$ into (VI). Diacetylcystic acid and Br in MeOH-CCl_4 give a *Br-lactone*, $\text{C}_{34}\text{H}_{51}\text{O}_6\text{Br}$, m.p. 184—190°, $[\alpha]_D^{25} +8.5^\circ$, $[\alpha]_{441}^{25} +12.1^\circ$ in dioxan. Me diacetylcystate with $\text{H}_2\text{O}_2\text{-AcOH-H}_2\text{O}$ at 70—80° gives a substance, $\text{C}_{35}\text{H}_{54}\text{O}_7$, m.p. 215—217.5°, $[\alpha]_D^{25} -74.2^\circ$, $[\alpha]_{441}^{25} -87.6^\circ$ in dioxan (no acetate or oxime). Regularities in $[\alpha]$ are noted, but not explained. R. S. C.

Vanguerin. New saponin from *Vangueria tomentosa*. K. W. MERZ and H. TSCHUBEL (Ber., 1939, 72, [B], 1017—1028).—Extraction of the root bark of *V. tomentosa* with boiling H_2O removes mannitol and a large proportion of brown extractives and the residue slowly yields *vanguerin* (I), $\text{C}_{41}\text{H}_{64}\text{O}_{11}$, m.p. 275—280° (decomp.) after softening at 255—260°, $[\alpha]_D^{25} -10.1^\circ$ in dioxan, to boiling EtOH . (I) is sol. in alkali hydroxide and is pptd. from this solution by CO_2 . It gives characteristic colour reactions with $\text{Ac}_2\text{O-80\% H}_2\text{SO}_4$ and with $\alpha\text{-C}_{10}\text{H}_7\text{-OH}$ and reduces Fehling's solution after being boiled with dil. HCl . It is converted by $\text{Ac}_2\text{O-NaOAc}$ or by Ac_2O in hot or cold $\text{C}_5\text{H}_5\text{N}$ into non-cryst. *vanguerin penta-acetate*, decomp. 184°; cryst. derivatives are not obtained from (I) and *BzCl*, *p*- or *m*- $\text{NO}_2\text{-C}_6\text{H}_4\cdot\text{COCl}$. (I) is hydrolysed by 4.5% HCl to *vanguerigenin* (II), $\text{C}_{30}\text{H}_{46}\text{O}_3$, m.p. 266°, $[\alpha]_D^{25} +191.3^\circ$ in CHCl_3 [*Ac* derivative (+1EtOH), m.p. 295°], *l*-arabinose, and *l*-rhamnose. (II) contains CO_2H since 2 active H atoms (Zerevitinov) are present and it is converted by KOH-MeI in MeOH at 100° into *vanguerigenin Me ester*, m.p. 195° (*Ac* derivative, m.p. 248°), which can be hydrolysed only with great difficulty. (II) gives an intense yellow colour with $\text{C}(\text{NO}_2)_4$ in CCl_4 ; in AcOH containing PtO_2 it absorbs $\sim 1\text{ H}_2$ giving a poorly cryst. product with ill-defined m.p. It is stable towards KMnO_4 but reacts with Br in CCl_4 or AcOH evolving HBr and giving small amounts of an uninvestigated *Br*-compound, m.p. 263—265°. When heated above its m.p., (II) loses CO_2 giving the non-acidic *vanguerol* (*decarboxyvanguerigenin*), $\text{C}_{29}\text{H}_{46}\text{O}$, m.p. 207°, which gives a yellow-brown colour with $\text{C}(\text{NO}_2)_4$ in CHCl_3 , immediately decolorises alkaline KMnO_4 , and gives a cryst. additive product with Br. Strong acids, e.g., HCl , isomerise (II) to *vanguerigenin*.

lactone, $C_{30}H_{46}O_3$, m.p. 281° [*Ac* derivative, prisms, m.p. 314° , from $CHCl_3$ or Et_2O and cubes, m.p. 325° , from $AcOH$; does not contain active H (Zerevitinov)]. Dehydrogenation (Se) of (II) leads to 1:2:7- $C_{10}H_5Me_3$. (II) is therefore a triterpene, and the foaming power and colour reactions of (I) cause it to be regarded as a saponin the aglucon of which has the picene skeleton. In properties there is a great similarity between (I), oleanolic acid, and hederagenin. (I) is therefore regarded provisionally as dedihydro-oleanolic acid or an isomeride thereof. H. W.

Pyroabietic acids. R. LOMBARD (Compt. rend., 1939, 208, 1321—1323).—Abietic acid (I) when heated with Pd-C gives (cf. Fleck and Palkin, A., 1939, II, 30) dehydroabietic acid, m.p. 173° , $[\alpha]_D^{20} +62^\circ$ (*Me* ester, m.p. 59° , $[\alpha]_D^{20} +62^\circ$), identical with that obtained from (I) (1 mol.) and SeO_2 (0.5 mol.) in cold $EtOH/10$ days. (I) with Pd-C- H_2 at $250^\circ/100$ kg. gives a dihydroabietic acid, m.p. 176° , $[\alpha]_D^{20} +107^\circ$. (I) with Raney Ni- H_2 at $250^\circ/100$ kg. gives a tetrahydroabietic acid, m.p. 170° , $[\alpha]_D^{20} +47^\circ$, the X-ray spectrum of which differs from that of pyroabietic acid (II). When (I) is heated with Pd-C, only (II) is formed. J. L. D.

Dibromodihydroabietic acid. T. HASSELSTROM and J. D. MCPHERSON (J. Amer. Chem. Soc., 1939, 61, 1223—1230).—Abietic acid (from rosin), m.p. 171 — 174° , $[\alpha]_D -99^\circ$ in $EtOH$, with $HBr-AcOH$ at 0° gives dibromodihydroabietic acid, m.p. 172 — 173° (decomp.), $[\alpha]_D 0^\circ$ to $+29.2^\circ$ in $EtOH$, converted by hot $AcOH$ into an acid, $C_{20}H_{30}O_2$, m.p. 168 — 171° , $[\alpha] -90.0^\circ$ in $EtOH$ (di-*n*-amylamine salt, m.p. 136 — 138.5° , $[\alpha]_D -44.5^\circ$ in $EtOH$), and by $Na-EtOH$ into dihydroabietic acid, m.p. 217.5 — 218.5° , $[\alpha]_D -23^\circ$ in dry Et_2O (di-*n*-amylamine salt, m.p. 121.5 — 122° , $[\alpha]_D -24^\circ$ in dry Et_2O ; *Me* ester, m.p. 131.5 — 132.5° , $[\alpha]_D -21.5^\circ$ in dry Et_2O). M.p. are corr. Refined ψ -pimaric (dihydroabietic) acid is obtained having m.p. 195.5 — 198° , $[\alpha]_D +0.33^\circ$. R. S. C.

Active principles of leguminous fish-poison plants. I. Properties of *l*- α -toxicarol isolated from *Derris malaccensis* (Kinta type). S. H. HARPER (J.C.S., 1939, 812—816).—The optically active precursor of toxicarol has been obtained by direct crystallisation of an ethereal extract of *D. malaccensis*. After removal of sumatrol, the *l*- α -toxicarol (I) was identical in properties with that described by Tattersfield and Martin (B., 1937, 728). It is concluded that the optical data of Cahn *et al.* (B., 1938, 1098) are untrustworthy, and their criticism is unjustified. Racemisation of (I) in C_6H_5-MeOH by $KOH \propto$ the amount of $MeOH$ added with the alkali. F. R. S.

Rottlerin. H. BROCKMANN and K. MAIER (Naturwiss., 1939, 27, 259—260; cf. A., 1938, II, 108, 334).—Under the action of weak alkali isorottlerin (I) is transformed into an isomeride (II), m.p. 194° . This is converted by Me_2SO_4 into a *Me*₅ ether (III), $C_{30}H_{42}O_3(OMe)_5$, m.p. 136° , which is hydrogenated to a H_4 -compound (IV), m.p. 98° . Dehydroisorottlerin (V) and weak alkali afford a H_2 -isomeride (VI), m.p. 215° or 207° , which passes successively into (III) and (IV). (I) gives a H_4 -derivative, m.p.

225° , also obtained by hydrogenation (Pd-black) of (II) or (VI), of (I) with Pd-black in the presence of a little alkali carbonate, or of (V) in presence of Pt; it is methylated to (IV). H. W.

Condensation accompanying reduction. Z. C. GLACET and J. WIEMANN (Compt. rend., 1939, 208, 1233—1234).— $CH_2=CH-CHO$ with $AcOH-Mg$ gives a mixture of 2-hydroxy- and 4-hydroxy-5-vinyl-tetrahydrofuran, b.p. $79^\circ/12$ mm. (acetate, b.p. 88 — $89^\circ/13$ mm.). The terminal double linking is indicated by the Raman spectrum. J. L. D.

Condensation accompanying reduction. Z. C. GLACET (Compt. rend., 1939, 208, 1323—1325).— $CHMe:CHO$ with $Mg-AcOH$ gives 4-hydroxy-2-methyl- (I), b.p. 106 — $107^\circ/13$ mm. (acetate, b.p. 109.5 — $110^\circ/12$ mm., easily hydrolysed by cold H_2O), which quickly resinifies in air, and 2-hydroxy-4-methyl-5-propenyl-2:3:4:5-tetrahydrofuran (II), b.p. 113 — $115^\circ/15$ mm. (acetate, b.p. 115 — $116^\circ/13$ mm.), unstable in air. (I) and (II) with $H_2C_2O_4$ or $CuSO_4$ give 2-methyl-5-propenyl-2:3-dihydrofuran, b.p. 58 — $59^\circ/40$ mm., and 4-methyl-5-propenyl-4:5-dihydrofuran, b.p. 58.5 — $59^\circ/13$ mm., respectively, each of which reacts with 2 Br. The structures are confirmed by Raman spectrum measurements. J. L. D.

Preparation of 2- and 3-hydroxyfuran. H. H. HODGSON and R. R. DAVIES (J.C.S., 1939, 806—809).— Na_2 5-sulphofuroate with $NaOH$ and a trace of $KClO_3$ at 200° gives 2-hydroxyfuran, m.p. 80° , decomp. 90° . Bromination of furoic acid in $CHCl_3$ affords 2-bromo-3-hydroxyfuran, m.p. 85° , dehalogenated ($Na-Hg$) to 3-hydroxyfuran, m.p. 58° , which with maleic anhydride yields 4-hydroxy-3:6-endoxo- Δ^4 -tetrahydrophthalic anhydride, m.p. 132° (decomp.); the anhydride and HBr give 4-hydroxyphthalic acid. F. R. S.

Ethynylfurfuryl alcohol.—See B., 1939, 578.

Methylfurfurylpropionic acid. O. WICHTERLE (Coll. Czech. Chem. Comm., 1939, 11, 171—175).— γ -Diketo-octoic acid distilled with $EtOH-C_6H_6$ gives its *Et* ester, b.p. 154.5 — $155^\circ/9.5$ mm., and some *Et* β -5-methylfurfuryl-2-propionate, b.p. 102 — $102.5^\circ/9.5$ mm., hydrolysed to the corresponding acid (I), m.p. 61 — 62° (amide, m.p. 99 — 100°). 5-Methylfurfuraldehyde, Ac_2O , and $NaOAc$ give the acrylic acid, reduced by $Na-Hg$ to (I). R. S. C.

Condensation of furan derivatives. IX. Eutectics of ketone-phenol systems, and the formation amongst them of oxonium complexes. V. V. TSHELINCEV and V. and G. KUZNETZOV (J. Gen. Chem. Russ., 1939, 9, 160—166).—The fusion diagrams exhibit max. corresponding with 2:1 compounds in the systems furfurylideneacetone-*p*- $C_6H_4(OH)_2$ (I), m.p. 33° , benzylideneacetone (II)-*o*- $C_6H_4(OH)_2$ (III), m.p. 51° , (II)-*m*- $C_6H_4(OH)_2$ (IV), m.p. 39° , (II)-(I), m.p. 81° , difurfurylideneacetone (V)-(IV), m.p. 63° , and (V)-(I), m.p. 82.5° , and with 1:1 compounds in the systems (V)-(III), m.p. 67 — 69° , dibenzylideneacetone (VI)-(III), m.p. 79° , (VI)-(IV), m.p. 97.5° , and (VI)-(I), m.p. 99° . R. T.

Reactivity of two diene systems of furylethylene. R. PAUL (Compt. rend., 1939, 208, 1028—

1030; cf. van Campen and Johnson, A., 1933, 280).—Equimol. amounts of furylethylene (I) with maleic anhydride (II) in Et₂O at room temp. afford the *anhydride* (?), m.p. 150°, of 3:4:5:6-tetrahydrobenzofuran-3:4-dicarboxylic acid, which with aq. Na₂CO₃ and then HCl gives 3:4:5:6-tetrahydrobenzofuran-3:4-dicarboxylic acid, m.p. 227–228°, which is stable to boiling H₂O, absorbs 4 H (H₂-Pt or -Raney Ni) with difficulty, and gives no CH₂O with O₃, which indicates that the extranuclear double linking in (I) is involved in the reaction. Furylethane with (II) affords the *anhydride*, m.p. 97–98°, of 1:4-oxido-1-ethyl-Δ²-cyclohexene-5:6-dicarboxylic acid, easily hydrolysed by boiling H₂O, and with H₂-Raney Ni rapidly affords the *anhydride*, m.p. 108°, of 1:4-oxido-1-ethylcyclohexane-5:6-dicarboxylic acid. J. L. D.

Preparation of *dl*-α-tocopherol from synthetic chimol. P. KARRER and B. H. RINGIER (Helv. Chim. Acta, 1939, 22, 610–616).—Hexahydro-γ-ionone, CH₂Br·CO₂Et, and Cu–Zn in PhMe yield *Et* β-hydroxy-β₂κ-trimethyldodecoate, b.p. 183°/12 mm., converted by successive treatments with HBr at 100° and Zn–Cu in 80% AcOH at 120° followed by hydrogenation (Pt) into *Et* β₂κ-trimethyldodecoate. This is reduced (Bouveault–Blanc) to hexahydrofarnesol, converted by PBr₃ or by HBr at 130–140° into hexahydrofarnesyl bromide, which is transformed by successive treatments with CHAcNa·CO₂Et and KOH into β₂κ-trimethylpentadecan-β-one, b.p. 166–173°/10 mm., in very modest yield. This is transformed by NaNH₂ and C₂H₂ into γγλ-tetramethyl-Δ²-hexadecin-γ-ol, partly hydrogenated (Pt) to the corresponding ethylenic compound, which is transformed by PBr₃ into phytyl bromide (I). Trimethylquinol and (I) in ligroin containing ZnCl₂ afford synthetic *dl*-α-tocopherol. The allophanate derived therefrom has m.p. ~4° < that observed for the natural derivative; it is uncertain whether this is due to the presence of an obstinate impurity or is caused by steric difference. There is no difference in the physiological activity of the two materials. H. W.

Lower homologues of α-tocopherol. Oxidation products of compounds resembling tocopherol. P. KARRER, H. FRITZSCHE, and R. ESCHER (Helv. Chim. Acta, 1939, 22, 661–665).—*dl*-7:8-Dimethyltolcol is converted into the *acetate*, b.p. 150–160°/0.01–0.005 mm., and *allophanate*, m.p. 146°. Evidence is adduced in favour of the view that “γ-” is somewhat impure β-tocopherol. 2:3:5-Trimethyl-5-β-hydroxypropyl-*p*-benzoquinone (I) is reduced by Zn dust and AcOH at 100° to 2:3:5-trimethyl-6-β-hydroxypropylquinol (II), m.p. 137° (*triacetate*, m.p. 94°). Reduction of (I) to (II) is also effected with Zn dust–AcOH–HBr. H. W.

Higher homologue of α-tocopherol. P. KARRER and O. HOFFMANN (Helv. Chim. Acta, 1939, 22, 654–657).—3:5-Dimethyl-2-ethylphenol is converted by HCl and NaNO₂ in EtOH at 0° into 4-nitroso-3:5-dimethyl-2-ethylphenol, m.p. 165° (decomp.), transformed by H₂O₂ in boiling dil. HCl into 3:5-dimethyl-2-ethyl-*p*-benzoquinone, reduced by Zn and AcOH at 100° to 3:5-dimethyl-2-ethylquinol (I), m.p. 157°. This is condensed by ZnCl₂ in ligroin with

phytyl bromide to 5:7-dimethyl-8-ethyltolcol (II), an oil, which reduces cold AgNO₃ and AuCl₃ and gives a cryst. *allophanate*, m.p. 170–171°. In doses of 16 mg. (II) has full vitamin-E activity. Allyl bromide, (I), and ZnCl₂ in boiling C₆H₆ afford 5-hydroxy-2:4:6-trimethyl-7-ethylcoumaran, m.p. 111°. The prep. of cumoquinone is described. H. W.

7-Coumaronyloxyacetic acid.—See B., 1939, 568.

Two 4-aminocoumarans. P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1939, 22, 657–660).—1-Methylcoumaran is coupled with diazotised 2:4-(NO₂)₂C₆H₃NH₂ in AcOH to 4:2:4'-dinitrobenzeneazo-1-methylcoumaran, reduced (Pt in AcOH–EtOH) to the cryst. 4-amino-1-methylcoumaran (*hydrochloride*), which reduces cold AgNO₃–EtOH. The NH₂ group can be diazotised and the salt is hydrolysed to 4-hydroxy-1-methylcoumaran, characterised as the *allophanate*, decomp. ~210° after softening. 4:2':4'-Dinitrobenzeneazo-1:3:6-trimethylcoumaran is similarly reduced to 4-amino-1:3:6-trimethylcoumaran, m.p. 113°. H. W.

Limited applicability of Kostanecki's reaction. Influence of halogen atoms on the reaction. D. CHAKRAVARTI and B. MAJUMDAR (J. Indian Chem. Soc., 1939, 16, 151–159).—1:3:6-C₆H₃MeCl·OAc and AlCl₃ yield 5-chloro-2-hydroxy-3-methylacetophenone (I), m.p. 70° [*semicarbazone*, m.p. 233° (decomp.)]. Similarly, from the propionyl derivatives of the appropriate phenols are prepared 5-chloro-2-hydroxy-3-methyl- (II), m.p. 61° (*semicarbazone*, m.p. 205°), 3-chloro-4-hydroxy-, m.p. 80° (Ac derivative, b.p. 155°/6 mm.), 3-bromo-4-hydroxy- (III), m.p. 130° and 5-bromo-2-hydroxy-propionophenone (IV), m.p. 78°. Heated at 170–180° for 12 hr. with NaOAc–Ac₂O, (I), 2:3:5:1-OH·C₆H₂MeCl·COMe (V), (II), 2:3:5:1-OH·C₆H₂MeCl·COEt (VI), 2:5:1-OH·C₆H₃Cl·COEt (VII), and (IV) yield respectively 6-chloro-2:8-, m.p. 139°, and 8-chloro-2:6-dimethyl-3-acetylchromone, m.p. 131°, 6-chloro-2:3:8- and 8-chloro-2:3:6-trimethylchromone, 6-chloro-2:3- and 6-bromo-2:3-dimethylchromone. (II), (VI), and (VII) also yield styryl derivatives. Similarly with EtCO₂Na and (EtCO)₂O, (I), (V), (II), (VI), (IV), and (VII) yield respectively 6-chloro-3:4:8-trimethylcoumarin, b.p. 180–200°/6 mm., m.p. 94°, 8-chloro-3:4:6-trimethylcoumarin, 6-chloro-3:8- (VIII), m.p. 85°, 8-chloro-3:6-dimethyl-, m.p. 74–75°, 6-bromo-, m.p. 87°, and 6-chloro-3-methyl-, m.p. 65–66°, -2-ethylchromone. The last-named is also formed by the interaction of 2:5:1-OH·C₆H₃Cl·COMe and EtCO₂Et with Na followed by heating with AcOH–HBr. Hydrolysis of (VIII) with NaOEt gives (II). With PrCO₂Na and (PrCO)₂O, (II), (VI), (VII), and (IV) give respectively 6-chloro-3:8-, m.p. 95°, and 8-chloro-3:6-dimethyl-, m.p. 68–71°, 6-chloro-, m.p. 85°, and 6-bromo-3-methyl-, m.p. 83–84°, -2-propylchromone. Kostanecki's reaction therefore proceeds normally except in the case of *o*-hydroxyacetophenones heated with EtCO₂Na and (EtCO)₂O, when coumarins are formed. J. D. R.

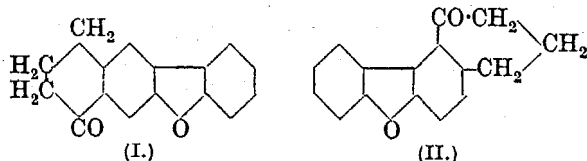
Natural coumarins. XLVI. Synthesis of seselin. E. SPÄTH and R. HILLEL (Ber., 1939, 72, [B], 963–965).—Seselin, m.p. 118–119°, is obtained

by heating umbelliferone with β -methyl- Δ^7 -butin- β -ol at 200° vac. H. W.

Pechmann dyes. Mechanism of formation of the mono-acid by hydrolytic fission. P. CHOVIN (Compt. rend., 1939, 208, 1228—1230; cf. A., 1939, II, 113).—Graded alkaline hydrolysis of the Pechmann dye (I) derived from α -naphthoylmethyl- α' -benzoylmethylfumaric acid (II), m.p. 272° (decomp.; block), affords 6-naphthyl-3-benzoylmethyl-1:2-pyrone-4-carboxylic acid (III), m.p. 246° (decomp.; block), converted by Ac_2O into (I). As partial cyclisation of (II) also affords (III), it follows that (III) is formed in each reaction from (II). Closure of both rings in (II) gives a yellow isomeride, m.p. 305°, of (I).

J. L. D.

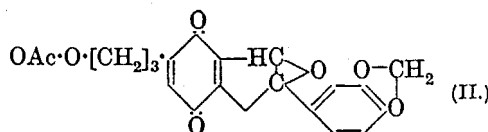
Amino-ketones derived from tetrahydrobenz[b]naphtho[2:3-d]furan. R. A. ROBINSON and E. MOSETTIG (J. Amer. Chem. Soc., 1939, 61, 1148—1151).— γ -3-Dibenzfuryl- n -butyric acid and P_2O_5 in 85% H_3PO_4 at 170° afford 50% of 7-keto-7:8:9:10-tetrahydrobenz[b]naphtho[2:3-d]furan (I), m.p. 137—138° [semicarbazone, m.p. 260—265° (decomp.)], and 3—4% (more actually formed) of 1-keto-1:2:3:4-tetrahydrobenz[b]naphtho[1:2-d]furan (II),



m.p. 112—113° (oxime, m.p. 200—203°). N_2H_4 and NaOEt-EtOH at 170° convert (I) into 7:8:9:10-tetrahydrobenz[b]naphtho[2:3-d]furan, m.p. 75—77° (picrate, m.p. 139—141°; Clemmensen reduction gives a 5—10% yield with 40—50% of a substance, m.p. ~190—210°, converted by Se into brazan, whence its structure follows. $\text{Br-Et}_2\text{O}$ converts (I) into the 8-*Br*-derivative, m.p. 207° (decomp.), which with the appropriate *sec.* base in C_6H_6 at 100° or the b.p. yields the hydrochlorides, m.p. 208—212° (decomp.), 235—237° (decomp.), and 206—210° (decomp.), of the 8-dimethylamino- (III), 8-piperidino- (IV), and 8-1':2':3':4'-tetrahydroisoquinolino-ketones, respectively; some (I) is also obtained and traces of (?) 7-hydroxybrazan. The hydrochlorides are rather unstable. Attempts to reduce (III) and (IV) to *sec.* alcohols failed. The NEt_2 -ketone could not be prepared. Prep. of 6- ω -bromoacetyl-1:2:3:4-tetrahydrodibenzfuran, the derived NH_2 -ketones, 6- β -dimethylamino-, an oil, 6- β -piperidino-, m.p. 129—131°, and 6-1':2':3':4'-tetrahydroisoquinolino- α -hydroxyethyl-1:2:3:4-tetrahydrodibenzfuran, m.p. 144.5—145.5°, is described (cf. A., 1936, 733). R. S. C.

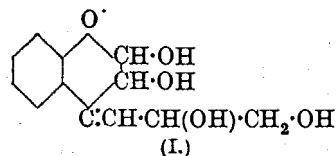
Egonol. VIII. Noregonolonidin acetate and intensely coloured compounds formed therefrom. S. KAWAI, K. SUGIMOTO, and N. SUGIYAMA [with, in part, E. YAMAMOTO, S. YOSIDA, and T. NAKAMURA] (Ber., 1939, 72, [B], 953—962).—Egonol benzoate is oxidised by 30% H_2O_2 in AcOH at 50—55° to noregonolonidin benzoate, m.p. 226—227°, which forms wine-red solutions; it is reduced (Pt-black in

dioxan) to 4:7-dihydronoregonolonidin benzoate, colourless needles, m.p. 196.5—197.5° to a dark red melt. Finely-divided noregonolonidin acetate (I) is oxidised by 30% H_2O_2 in faintly alkaline COMe_2 to 2:3-oxido-2:3-dihydronoregonolonidin acetate (II), which

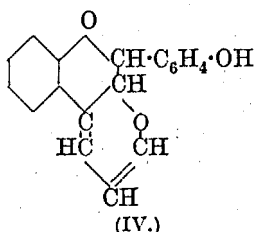
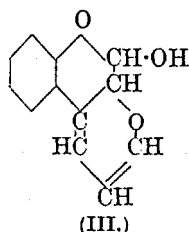


does not give a colour with $\text{Cu}(\text{OAc})_2$ or FeCl_3 in EtOH and affords a negative Legal test. $\text{NHPh}\cdot\text{NH}_2$ causes only blackening, thus indicating the quinonoid nature of (II); the oxime decomposes at 180°. CH_2N_2 in Et_2O transforms (II) into 2:3-oxido-6-methyl-2:3-dihydronoregonolonidin acetate, m.p. 141.5—142°, from which OMe is absent (Zeisel). HCl in dry $\text{CHCl}_3\text{-Et}_2\text{O}$ converts (II) into 3-hydroxy- (III), m.p. 222°, and 3-chloro-, m.p. 166.5°, -noregonolonidin acetate. Hydrogenation (PtO_2 in EtOAc) of (II) follows a complex course, giving the colourless 2-hydroxytetrahydronoregonolonidin acetate, m.p. 175—175.5°, and a pale yellow substance, m.p. 172—175.5°, solutions of which in org. media have a blue fluorescence. With Zn dust and AcOH (II) gives (III) and (I). Reducing acetylation (Zn dust and Ac_2O) of (I) yields 4:7-di-acetoxy-2-3':4'-methylenedioxyphenyl-5- ω -acetoxy- n -propylcoumarone, m.p. 111°, also obtained by similar treatment of (II). The dark colour of compounds of the noregonolonidin series is ascribed to the presence of a double linking between $\text{C}_{(2)}$ and $\text{C}_{(3)}$, thus giving an uninterrupted conjugated system between the double linkings of the benzoquinone and those of the methylenedioxyphenyl nucleus. If this is absent there is only a yellow colour due to the quinonoid nucleus. The author's conception of the formation of flavylum salts (A., 1939, II, 222) differs from that of Robinson only in respect of the chalkone stage, Robinson regarding an oxonium, the author a carbonium, compound as intermediate. H. W.

Sugar-phenol condensations. Condensation of *d*-glucose with phenol. J. B. NIEDERL and R. K. MAURMEYER (J. Amer. Chem. Soc., 1939, 61, 1005—1010).— PhOH , anhyd. *d*-glucose, and (a) HCl-AcOH (2 days) or (b) aq. HCl (1 month) give substances, (I) $\text{C}_{12}\text{H}_{14}\text{O}_5$, + H_2O , m.p. 115° (decomp.), $[\alpha]_D^{25} +79.2^\circ$ in H_2O {with conc. HNO_3 gives picric acid (II); tetrabenzoate, + H_2O , m.p. 130°; *Na* salt; phenylosazone, + H_2O , m.p. 183°; dibromide, m.p. 130° (decomp.) [with conc. HNO_3 gives (II); tetrabenzoate, m.p. 155°; semicarbazone, m.p. 210°; 2:4-dinitrophenylhydrazone, m.p. 181°; $(\text{NO}_2)_x$ -derivative, + H_2O , m.p. 107° (decomp.)], (III) $\text{C}_{12}\text{H}_{10}\text{O}_3$ (impure), and (IV) $\text{C}_{18}\text{H}_{14}\text{O}_3$, m.p. 238—240° (benzoate, m.p. 169°; phenylurethane, m.p. 195°). Zn-AcOH reduces (III) to an amorphous compound, $\text{C}_{12}\text{H}_{12}\text{O}_3$, + H_2O , m.p. 120° (decomp.) [benzoate, + H_2O , m.p. 145°; *p*-nitrobenzoate, m.p. 175°; di-



bromide, m.p. 138° (decomp.); (NO_2)₃-derivative, m.p.



130° (decomp.). The annexed and similar structures are discussed. R. S. C.

Action of bromine on nitrothiophen. V. S. BABASINIAN (J. Amer. Chem. Soc., 1938, 60, 2906—2909).—2-Nitrothiophen (50 g.) and Br vapour at room temp. (30 days) give 2-bromo- (I), m.p. 47—48° (8.5 g.), and 2:3-dibromo-5-nitrothiophen (II), m.p. 75.5—76° (6 g.), 2:5-dibromo-3-nitrothiophen, m.p. 61° (0.8 g.; produced from 3-nitrothiophen, present as impurity), tetrabromothiophen (10 g.), and traces of other derivatives. The NO_2 in (I) is more firmly held than that in (II). R. S. C.

Valency angle. II. Angle at the sulphur atom attached to phenyl. A. LÜTTRINGHAUS [with, in part, K. HAUSCHILD] (Ber., 1939, 72, [B], 887—897).—It is shown qualitatively by comparison of yields that CH_2 and S compounds behave very similarly. The somewhat lower yields of the latter substances are due to the fact that the union $\text{S}\cdot\text{C}_{\text{arom.}}$ is somewhat longer than $\text{C}_{\text{aliph.}}\cdot\text{C}_{\text{arom.}}$; with approx. the same valency angle at CH_2 or S, this involves an increase in the O—O distance which has to be bridged. The ring system with O as central atom requires a bridge greater by about two CH_2 groups for successful intramol. ring-closure. The angle at O is therefore \gg that at S or CH_2 . SOCl_2 and PhOH in CHCl_3 at room temp. yield (*p*- $\text{OH}\cdot\text{C}_6\text{H}_4$)₂S (I), m.p. 150°, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, and tri-*p*-hydroxyphenylsulphonium chloride, m.p. 273° when rapidly heated [normal sulphate, m.p. 287° (decomp.)]. The change is probably $[(\text{OH}\cdot\text{C}_6\text{H}_4)_2\text{S}\cdot\text{OH}]\text{Cl} + \text{PhOH} \rightarrow \text{H}_2\text{O} + [(\text{HO}\cdot\text{C}_6\text{H}_4)_2\text{S}]\text{Cl}$ or $\rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_4\text{Cl}\cdot\text{OH} + (\text{I})$, or alternatively $[(\text{OH}\cdot\text{C}_6\text{H}_4)_2\text{S}\cdot\text{Cl}]\text{Cl} + \text{PhOH} \rightarrow \text{HCl} + \text{C}_6\text{H}_4\text{Cl}\cdot\text{OH} + (\text{I})$. Gradual addition of $\text{KOH}\cdot\text{MeOH}$ to a boiling solution of (I) and $\text{Br}\cdot[\text{CH}_2]_{10}\cdot\text{Br}$ in boiling EtOH gives *p*-hydroxy-*p'*- κ -bromoundecoxydiphenyl sulphide (II), m.p. 59—61°. *p*-Hydroxy-*p'*- δ -bromo-octyloxy-, m.p. 48.5—50°, and *p*-hydroxy-*p'*- ζ -bromohexyloxy- (III), m.p. 50—53°, diphenyl sulphide are similarly obtained. (II), dissolved in amyl alcohol, is added very slowly to a boiling suspension of K_2CO_3 in the same solvent; the residue, after removal of the solvent, is extracted with boiling C_6H_6 -petroleum and the solution is extracted with Claisen's alkali, thus giving 4:4'-dihydroxydiphenyl sulphide decamethylene ether,

$\text{S} \begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \text{C}_6\text{H}_4\cdot\text{O} \end{smallmatrix} [\text{CH}_2]_{10}$, m.p. 66.5°, which is indifferent towards MgMeI in abs. amyl ether, is incompletely hydrolysed by boiling 48% $\text{HBr}\cdot\text{Ac}_2\text{O}$ with production of $\text{Br}\cdot[\text{CH}_2]_{10}\cdot\text{Br}$, and is smoothly transformed by AlBr_3 in boiling C_6H_6 into (I). It is oxidised by $\text{o}\cdot\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ to the corresponding sulphone,

m.p. 144.5°. 4:4'-Dihydroxydiphenyl sulphide octamethylene ether, m.p. 53°, is prepared similarly in 15.8% yield; the sulphone has m.p. 174.5°. Under the same conditions (III) affords dimeric 4:4'-dihydroxydiphenyl sulphide hexamethylene ether, m.p. 148°. H. W.

Valency angle. IV. Determination of linking angles by chemical methods. A. LÜTTRINGHAUS and R. KOHLHAAS (Ber., 1939, 72, [B], 907—913).—It is shown that the angle at X in compounds $\text{X} \begin{smallmatrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \text{C}_6\text{H}_4\cdot\text{O} \end{smallmatrix} [\text{CH}_2]_n$ ($\text{X} = \text{CH}_2$, O or S) can be determined from measurement of the yields obtained by ring-closure of $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_n\cdot\text{Br}$ if the angle is determined in a single case by an independent method. The angle at S in (*p*- $\text{OH}\cdot\text{C}_6\text{H}_4$)₂S is $112.4^\circ \pm 1.5^\circ$ as determined röntgenographically. For CH_2 and O in the above cyclic compounds the vals. are $110^\circ \pm 3^\circ$ and $129^\circ \pm 4^\circ$, respectively. H. W.

Dyes derived from acenaphthenequinone. VII. 2-(5-Chloro)thionaphthenacenaphthyleneindigos. S. H. GUHA (J. Indian Chem. Soc., 1939, 16, 127—130).—5-Chloro-3-hydroxythionaphthen (I) with acenaphthenequinone in $\text{AcOH}\cdot\text{HCl}$ yields 2-(5-chloro)thionaphthenacenaphthyleneindigo (II). Similarly from (I) and 3-chloro-, 3-bromo-, or 1-methoxy-acenaphthene and phenanthraquinone are obtained, respectively, 2-(5-chloro)thionaphthen-8'-(3'-chloro)- (III), -(3'-bromo)- (IV), and -(1'-methoxy)-acenaphthyleneindigo (V) and 2-(5-chloro)thionaphthen-9'-phenanthreneindigo. (II) dyes wool and cotton dark red, (III) and (IV) dye wool brownish-red and cotton dark red, and (V) dyes wool light red. J. D. R.

Onium compounds. XXI. Pyrrolidinium analogues of choline and betaine. R. R. RENSHAW and W. E. CASS (J. Amer. Chem. Soc., 1939, 61, 1195—1198; cf. A., 1939, II, 226).—Na in EtOH, first boiling and then at 130°, reduces Et hygrate, b.p. 74—76°/12 mm., 2-acetyl- and 2-*n*-propionylpyrrole to 1-methyl-2-hydroxymethyl- (I), b.p. 67—68°/12 mm. [aurichloride, m.p. 203—207° (decomp.); picrate, m.p. 173—174° (decomp.)], 2- α -hydroxyethyl-, b.p. 97—102°/21 mm., 188—196°/760 mm. (picrate, m.p. 122—130°), and 2- α -hydroxy-*n*-propyl-, m.p. 48—50°, b.p. 96—102°/18 mm. (picrate, m.p. 124—130°), -pyrrolidine, respectively. (I) gives a methiodide, m.p. 283—284° (decomp.; uncorr.) (acetate, m.p. 127—128°), an acetate hydrochloride, hygroscopic, m.p. 73—74°, acetate hydrobromide, hygroscopic, m.p. 74—75°, and benzoate hydrochloride, m.p. 162—163°. $\text{MeI}\cdot\text{Ba}(\text{OH})_2$ in hot MeOH converts the other alcohols into 1:1-dimethyl-2- α -hydroxyethyl-, m.p. 111—123° and 127—138° (acetate, m.p. 129—140°), and 1:1-dimethyl-2- α -hydroxy-*n*-propyl-pyrrolidinium iodide, m.p. 106—113° (acetate, m.p. 166—170°). $\text{H}_2\cdot\text{PtO}_2$ in 20—50% aq. EtOH containing a slight excess of HCl or $\text{H}_2\cdot\text{Raney Ni}$ in EtOH at 150—160°/130—150 atm. reduces 2-methylcarbamyl-1-methylpyrrole to hydr-*N*-methylamide (70—90% yield) (hydrochloride, m.p. 146.5—148°; methiodide, m.p. 130—132.5°), hydrolysed by HCl at 125° to hygric acid, the Me ester (hygroscopic hydrobromide, m.p. 108—109.5°; methiodide, m.p. 103.5—104°) of which is obtained by HCl-MeOH in 60—65% yield and

with $\text{NH}_3\text{-MeOH}$ at $70\text{--}80^\circ$ gives 90% of *hygramide*, m.p. $135.5\text{--}137^\circ$ [*auri-*, m.p. $173\text{--}174^\circ$ after sintering, *platini-*, m.p. $196\text{--}197^\circ$ (decomp.), and *hydrochloride*, m.p. $192\text{--}193^\circ$; *picrate*, m.p. $132.5\text{--}133.5^\circ$; *methiodide*, m.p. $133\text{--}135^\circ$]. *Et hygrate hydrobromide*, hygroscopic, m.p. $83.5\text{--}85^\circ$, and *methiodide*, m.p. $88\text{--}89^\circ$, are also prepared. M.p. are corr.

R. S. C.

Reactions of hydrogen with pyrrole derivatives. II. J. L. RAINEY and H. ADKINS (J. Amer. Chem. Soc., 1939, 61, 1104—1110; cf. A., 1936, 861).— $1\text{-CO}_2\text{Et}$ greatly increases the ease of hydrogenation of pyrroles to pyrrolidines; 1-Bz may do so, but is often removed as $\text{CH}_2\text{Ph}\cdot\text{OH}$. This effect is due to electronic shifts. Hydrogenation of 2- or 3- CO_2Et -derivatives usually (one exception) occurs at the CO_2Et before the ring and yields Me derivatives, but occasionally the intermediate primary alcohols can be isolated. Reactions given below without description are hydrogenations in presence of Raney Ni, the solvent and temp. being stated in parentheses. 1-Carbethoxypyrrole (prep. by ClCO_2Et from K pyrrole in PhMe), b.p. $175\text{--}180^\circ/740\text{ mm.}$, gives (70° ; dioxan) 1-carbethoxypyrrolidine (93%). 1-Benzoylpyrrole (prep. from K pyrrole and BzCl in PhMe), b.p. $169\text{--}170^\circ/8\text{ mm.}$, gives (70° ; dioxan) 1-benzoxypyrrolidine (93%), b.p. $169\text{--}170^\circ/8\text{ mm.}$ *Et* 3:5-dimethyl-2:4-diethylpyrrole-1-carboxylate (this and other 1-derivatives similarly prepared from the 1-K derivative), b.p. $123\text{--}126^\circ/7\text{ mm.}$, gives (180° ; dioxan) *Et* 3:5-dimethyl-2:4-diethylpyrrolidine-1-carboxylate (87%), b.p. $119\text{--}121^\circ/7\text{ mm.}$ *Et*₃ 3:5-dimethylpyrrole-1:2:4-tricarboxylate, b.p. $158\text{--}160^\circ/1.2\text{ mm.}$, gives (180° ; dioxan) the derived pyrrolidine ester (I) (95%), b.p. $151^\circ/1.2\text{ mm.}$ *Et*₂ 3:5-dimethyl- (II), b.p. $156\text{--}158^\circ/11.5\text{ mm.}$, and -3:5-dimethyl-4-ethyl-pyrrole-1:2-dicarboxylate, b.p. $126\text{--}129^\circ/1\text{ mm.}$, give (120° ; 170° ; dioxan) 90% yield) *Et*₂ 3:5-dimethyl-, b.p. $146\text{--}147^\circ/11\text{ mm.}$, and 3:5-dimethyl-4-ethyl-pyrrolidine-1:2-dicarboxylate, b.p. $164\text{--}166^\circ/11\text{ mm.}$ When heated with conc. HCl at 150° and then esterified, (I) gives (II). *Et*₂ 2:4-dimethylpyrrole-1:3-dicarboxylate, m.p. $35\text{--}38^\circ$, b.p. $159\text{--}162^\circ/9\text{ mm.}$, gives (200° ; dioxan) the pyrrolidine ester (60%), b.p. $146\text{--}147^\circ/7\text{ mm.}$ *Et*₂ 1-benzoyl-3:5-dimethylpyrrole-2:4-dicarboxylate, m.p. $74\text{--}75^\circ$, b.p. $191\text{--}195^\circ/1\text{ mm.}$, gives (125° or 150° ; dioxan) $\text{CH}_2\text{Ph}\cdot\text{OH}$ (60%) and 2:4-dicarbethoxy-3:5-dimethylpyrrole (III) (85%). *Et* 1-benzoyl-2:4-dimethylpyrrole-3-carboxylate, m.p. $65\text{--}66^\circ$, b.p. $144\text{--}148^\circ/1\text{ mm.}$, gives (150° ; dioxan) $\text{CH}_2\text{Ph}\cdot\text{OH}$ (60%) and 3-carbethoxy-2:4-dimethylpyrrole (85%), m.p. $75\text{--}76^\circ$, b.p. $152^\circ/7\text{ mm.}$, also obtained by hydrolysing (III) by NaOH-EtOH and heating the product in glycerol at $145\text{--}155^\circ/7\text{ mm.}$ The products obtained (270° ; methylcyclohexane) from *Et*₂ 1-trimethylacetyl-3:5-dimethylpyrrole-2:4-dicarboxylate (prep. from the 1-K derivative by Bu^tCOCl in PhMe), m.p. $56\text{--}58^\circ$, b.p. $148\text{--}149^\circ/1\text{ mm.}$, were not identified. *Et* 2-acetylpyrrole-1-carboxylate, b.p. $119\text{--}121^\circ/7\text{ mm.}$, gives (140° ; dioxan) *Et* 2- α -hydroxyethylpyrrolidine-1-carboxylate (94%), b.p. $135\text{--}137^\circ/7\text{ mm.}$, or (80° ; dioxan) 15% thereof with 77% of *Et* 2-acetylpyrrolidine-1-carboxylate, b.p. $125\text{--}127^\circ/7\text{ mm.}$ (dinitrophenylhydrazone, m.p. $102\text{--}104^\circ$). *Et*

3-acetyl-2:4-dimethylpyrrole-1-carboxylate, b.p. $162\text{--}164^\circ/8\text{ mm.}$, gives (180° ; dioxan) *Et* 2:4-dimethyl-3- α -hydroxyethylpyrrolidine-1-carboxylate (80%), b.p. $166\text{--}171^\circ/8.5\text{ mm.}$, or (100° ; dioxan) *Et* 3-acetyl-2:4-dimethylpyrrolidine-1-carboxylate, b.p. $151\text{--}156^\circ/8.5\text{ mm.}$ (dinitrophenylhydrazone, m.p. $108\text{--}110^\circ$). *Et*₂ 4-acetyl-3:5-dimethylpyrrole-1:2-dicarboxylate, m.p. $74\text{--}76^\circ$, b.p. $161\text{--}165^\circ/1\text{ mm.}$, gives (180° ; EtOH) *Et*₂ 3:5-dimethyl-4- α -hydroxyethylpyrrolidine-1:2-dicarboxylate (71%), b.p. $165\text{--}170^\circ/1\text{ mm.}$ *Et*₂ 1:3:5-trimethylpyrrole-2:4-dicarboxylate (IV), m.p. $113\text{--}114^\circ$, b.p. $142\text{--}144^\circ/1\text{ mm.}$, gives (a) (Ni; 250° ; methylcyclohexane) 1:2:3:4:5-pentamethylpyrrolidine (V) (29%), b.p. $146\text{--}149^\circ/742\text{ mm.}$ [*picrate*, m.p. $192\text{--}193^\circ$ (decomp.)], and 57% of unchanged (IV), (b) (Cu chromite; 250° ; EtOH) 80% of (V), or (c) (Cu chromite; 220° ; EtOH) 23% of (V), 27% of (IV), and 36% of *Et* 1:2:3:5-tetramethylpyrrole-4-carboxylate, m.p. $72\text{--}73^\circ$, b.p. $121\text{--}125^\circ/1\text{ mm.}$ *Et*₂ 3:5-dimethyl-1-ethylpyrrole-2:4-dicarboxylate (prep. from the 1-Na derivative by Et_2SO_4), m.p. $39\text{--}39.5^\circ$, b.p. $145\text{--}148^\circ/1\text{ mm.}$, gives (250° ; methylcyclohexane) 19% of 2:3:4:5-tetramethyl-1-ethylpyrrolidine, 55% of ester being recovered. *Et* 2:4-dimethylpyrrole-3-carboxylate gives (220° ; EtOH) *Et* 2:4-dimethyl-1-ethylpyrrolidine-3-carboxylate (VI) (50%), b.p. $86\text{--}89^\circ/7\text{ mm.}$ (*picrate*, m.p. $110\text{--}112^\circ$; hydrochloride, m.p. $96\text{--}99^\circ$), 2:3:4-trimethyl-1-ethylpyrrolidine (VII) (10%), b.p. $147\text{--}150^\circ/740\text{ mm.}$ (*picrate*, m.p. $105\text{--}108^\circ$), and mixed pyrrolidones (12%, formed by ring-fission and re-closure, but with less catalyst in dioxan at 220° 15% of carbethoxypyrrolidines are formed; introduction of the 1-Et is due to the solvent EtOH. *Et* 2:4-dimethyl-1-ethylpyrrole-3-carboxylate (prep. from the 3:5-dicarboxylate), b.p. $138\text{--}141^\circ/7\text{ mm.}$, gives (220° ; EtOH) 78% of (VI) and 3% of (VII). *Et* 3:5-dimethylpyrrole-2-carboxylate (prep. from the 2:4-dicarboxylate by hydrolysing with H_2SO_4 at 50° and decarboxylating the product in glycerol), m.p. $124\text{--}125^\circ$, gives (220° ; EtOH) 2:3:5-trimethyl-1-ethylpyrrolidine, b.p. $139\text{--}142^\circ/740\text{ mm.}$ (*picrate*, m.p. $135\text{--}138^\circ$), 60% of the ester being unchanged. 2-Carbethoxypyrrole gives (220° ; EtOH) 2-methyl-1-ethylpyrrolidine (35%) and 2-hydroxymethyl-1-ethylpyrrolidine (14%), b.p. $75\text{--}81^\circ/11\text{ mm.}$ With $\text{H}_2\text{-Cu}$ chromite in EtOH at 190° (VI) gives 2:4-dimethyl-3-hydroxymethyl-1-ethylpyrrolidine (83%), b.p. $100\text{--}102^\circ/8\text{ mm.}$ (hydrochloride, m.p. $90\text{--}95^\circ$), and 3% of (VII). *Et*₂ 3:5-dimethylpyrrolidine-2:4-dicarboxylate, b.p. $140\text{--}142^\circ/7\text{ mm.}$, and 4-carbethoxy-3:5-dimethyl-1-ethylpyrrole-2-carboxylic acid, m.p. 137° , are described.

R. S. C.

Catalytic transformations of heterocyclic compounds. XI. Mechanism of simultaneous catalytic dehydrogenation of furan and furanidin (tetrahydrofuran) with *sec.* and *tert.* amines. J. K. JURIEV [with O. A. KANTSCHIEVA] (J. Gen. Chem. Russ., 1939, 9, 153—159).—Tetrahydrofuran (I)-amine mixtures passed over Al_2O_3 at 400° yield *N*-ethylpyrrolidine (II) (with NH_2Et 56, with NH_2Et_2 29, and with NEt_3 9% yield). The reactions are: (I) + $\text{NH}_2\text{Et} \rightarrow \text{OH}\cdot[\text{CH}_2]_4\cdot\text{NEt}_2$ (+ H_2O) \rightarrow $\text{OH}\cdot[\text{CH}_2]_4\cdot\text{NH}_2\text{Et} \rightarrow$ (II) + H_2O . Under the same

conditions (I) alone yields a variety of products, of which $\text{CHMe}:\text{CH}_2$ is identified. R. T.

Hydrogenations and dehydrogenations in the pyridine series. Model experiments for the mode of transportation of hydrogen by co-dehydrase. O. MUMM and J. DIEDERICHSEN (Annalen, 1939, 538, 195—236).—1:2-Dihydropyridines, the structure of which is proved by the prep. of some of them by hydrogenation of 2-methylene derivatives, are yellow, show no or yellowish-green fluorescence in ultra-violet light, are strongly basic and strongly reduce AgNO_3 and methylene-blue, and rapidly absorb 2 H but no more. 1:4-Dihydropyridines, including those prepared by the Hantzsch synthesis, are colourless, have blue fluorescence in ultra-violet light, are not or only slightly basic and reducing, and are difficultly reducible but then direct to the H_0 -stage. The products formed by reduction by activated Al are 1:2:1':2'-tetrahydro-2:2'-dipyridyls, the more stable isomerides being 1:2:1':2'-tetrahydro-4:4'-dipyridyls. Dihydropyridine is probably the 1:6- H_2 -derivative. Electronic interpretations of the reactions are offered. Reduction of the pyridinium methosulphate with $\text{Na}_2\text{S}_2\text{O}_4$ in aq. NaHCO_3 gives Et_2 1:2:6-trimethyl-1:4-dihydropyridine-3:5-dicarboxylate (I), m.p. 88°; reduction by Na-Hg and AcOH in H_2O - Et_2O gives similarly Et_2 4-phenyl-1:2:6-trimethyl-1:4-dihydropyridine-3:5-dicarboxylate (II), m.p. 131°. Et_2 4-phenyl-1:2:6-trimethyl-1:2-dihydropyridine-3:5-dicarboxylate (III) and maleic anhydride give the adduct, $\text{C}_{24}\text{H}_{27}\text{O}_7\text{N}$, m.p. 153°, but (II) does not react. Hydrogenation (PtO_2) of (II) and (III) in AcOH affords the piperidine derivative (picrate, m.p. 164°), and Se at 215° yields Et_2 4-phenyl-2:6-dimethylpyridine-3:5-dicarboxylate with loss of the 1-Me. Et_2 1:2:6-trimethyl-1:4-dihydropyridine-3:4-dicarboxylate, m.p. 54°, is obtained from the methosulphate by $\text{Na}_2\text{S}_2\text{O}_4$. Et_2 2:6-trimethyl-1:4-dihydropyridine-3:4-dicarboxylate (IV) is isomerised at 22° to the 1:2- H_2 -ester, gives a 1-Ac derivative, m.p. 119°, and is hydrogenated to the piperidine derivative, b.p. 160—163°/15 mm. (hydrochloride, m.p. 198°; platinichloride, m.p. 225—226°) (the H_4 -derivative could not be isolated after partial hydrogenation), which is hydrolysed by 5N-HCl to 2:6-dimethylpiperidine-3:4-dicarboxylic acid, m.p. 234°. N_2O_3 reacts as if (IV) had a 3- CH_2 , giving a bimol. product, $\text{C}_{26}\text{H}_{37}\text{O}_9\text{N}_3$, m.p. 162° (decomp.); $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ reacts similarly, but disproportionation also occurs and Et_2 3-p-nitrobenzylidene-2:6-dimethylpiperidine-3:4-dicarboxylate, m.p. 196° (decomp.), is isolated. The position of the H in Et 1:2-dimethyl-6-methylene-1:6-dihydropyridine-3-carboxylate is proved by its reaction with PhNCS without ring closure to give 1:6-dimethyl-2- β -anilino- β -thionethylidene-1:2-dihydropyridine-5-carboxylate, m.p. 70°. The 1:2- H_2 -analogue of (I) reacts with maleic anhydride, but the product is unstable, decomp. into succinic anhydride, and, presumably, the pyridine ester. Et_4 1:2:6:1':2':6'-hexamethyl-1:2:1':2'-tetrahydro-2:2'-dipyridyl-3:5:3':5'-tetracarboxylate (V) (prep. from the pyridine methosulphate by Na-Hg

and AcOH in H_2O), m.p. 168°, is converted by heating at 180° or by dry hot HCl-MeOH, but not by KOH-EtOH, into Et_4 1:2:6:1':2':6'-hexamethyl-1:2:1':2'-tetrahydro-4:4'-dipyridyl-3:5:3':5'-tetracarboxylate (VI), m.p. 193°. Oxidising agents (I, Br, etc.) convert (V) and (VI) into the unmol. pyridine derivatives. When heated, (V) and (VI) dissociate and lose H_2 or disproportionate. H_2 - PtO_2 converts the 2:6:2':6'- Me_4 analogue of (VI) into Et_2 2:6-dimethylpiperidine-3:5-dicarboxylate (picrate, m.p. 155°), hydrolysed to the corresponding acid (hydrochloride, m.p. 151°). H_2 - PtO_2 reduces (V) or (VI) to Et_2 1:2:6-trimethylpiperidine-3:5-dicarboxylate, an oil (picrate, m.p. 155°), hydrolysed to an acid, m.p. ~265° (decomp.) (mercurichloride, sinters at 160°, decomp. 167°), but an isomeric ester (picrate, m.p. 129°; hydrolysed to the same acid), is obtained from Et_2 2:6-dimethylpyridine-3:5-dicarboxylate methosulphate. The 2:6:2':6'- Me_4 analogue of (V) and HCl-MeOH give a mixture of the $\text{C}_5\text{H}_5\text{N}$ ester and Et_2 2:6-dimethyl-2:3-dihydropyridine-3:5-dicarboxylate, m.p. 101°. HCl-EtOH and (V) give the 2- CH_2 ester and Et_2 2:4:6-trimethyl-2:3-dihydropyridine-3:5-dicarboxylate, m.p. 69°.

R. S. C.

ω -Trichloro- and ω -dichloro- α -picoline. P. DYSON and D. L. HAMMICK (J.C.S., 1939, 781—782).—Chlorination of α -picoline in AcOH containing excess of KOAc gives ω -trichloro- α -picoline (I), b.p. 112—115°/15 mm., which is reduced ($\text{SnCl}_2\text{-HCl-COMe}$) to the ω - Cl_2 -compound (II), b.p. 90—92°/15—16 mm. Hydrolysis (H_2SO_4) of (I) yields picolinic acid and of (II) affords pyridine-2-aldehyde (2:4-dinitrophenylhydrazones, m.p. 213°).

F. R. S.

[Nitration of methyl homologues of pyridine.] E. PLAŽEK (Ber., 1939, 72, [B], 1126; cf. A., 1939, II, 226).—Nitrocollidine has been described previously by van Rijn (A., 1926, 525).

H. W.

4-Thiopyridone and derived substances. H. KING and L. L. WARE (J.C.S., 1939, 873—877).—4-Pyridone and P_2S_5 give 4-thiopyridone (I), m.p. 186° [picrate, m.p. 222° (decomp.)], which is methylated (MeI) to 4-methylthiopyridine, m.p. 44—45° (hydriodide, m.p. 170°; picrate, m.p. 245°; methiodide, m.p. 177°), oxidised (KMnO_4) to 4-methylsulphonylpyridine, m.p. 81°. $\text{CH}_2\text{Cl-CO}_2\text{H}$ and (I) afford pyridine-4-thioacetic acid, m.p. 270° (efferv.) (Na salt), whilst $\text{NaOH-H}_2\text{O}$ and (I) form Na pyridine-4-sulphonate (II) (+2 H_2O). PCl_5 and (II) do not give the desired pyridine-4-sulphonyl chloride but, depending on the method of working up, either 1:4'-pyridylpyridine-4-imine, m.p. ~160° [hydrochloride (+3.5 H_2O), m.p. 100°, anhyd., m.p. 280°; dinitrate, m.p. 226° (decomp.); mononitrate, m.p. 255° (decomp.); dipicrate (+ H_2O), m.p. 216°, anhyd., m.p. 227° (decomp.); diaurichloride, m.p. 280°], and some NH_4 pyridine-4-sulphonate, m.p. 257° (efferv.), or 1:4'-pyridyl-4-pyridone [picrate (+ H_2O), m.p. 202°; aurichloride (+2 H_2O), m.p. ~226°] (also isolated, 4-pyridone picrate, m.p. 240°, and 4-chloropyridine picrate, m.p. 146°). Cl_2 and (I) afford 4-chloropyridine and di-4-pyridyl sulphide, m.p. 71° (dipicrate, m.p. 229°), and Br and (I) yield di-4-pyridyl disulphide,

m.p. 74—75° (*dipicrate*, m.p. 231°; *zincichloride* (+0.5H₂O), m.p. >300°). F. R. S.

Structure of vitamin-B₆. I. E. T. STILLER, J. C. KERESZTESY, and J. R. STEVENS. II. S. A. HARRIS, E. T. STILLER, and K. FOLKERS (J. Amer. Chem. Soc., 1939, 61, 1237—1242, 1242—1244).—I. Vitamin-B₆ is shown to be probably 3-hydroxy-2-methyl-4:5-di(hydroxymethyl)pyridine (I). -B₆, C₈H₁₁O₃N, m.p. 159—160°, sublimes at 140—145°/10⁻⁴ mm., α 0, contains 3 active H, 1 C-Me, no OAlk or NAlk, gives a red FeCl₃ colour [cf. 3-hydroxypyridine (II)], is stable to acid and alkali, and is indifferent to HNO₃. It has *pK* (base) 6.2 × 10⁻¹⁰, compared with 6.0 and 1.7 × 10⁻¹⁰ for (II) and 2-pyridone, respectively. At *pH* 10.2 it has absorption max. at 2550 and 3260 Å., changing gradually to a single max. at 2920 Å. at *pH* 4; three derivatives of (II) show exactly similar absorption, but 2- and 4-pyridone behave differently. With CH₂N₂ in MeOH -B₆ gives a Me ether, m.p. 101—102° (*hydrochloride*, m.p. 147—148°) (cf. Kuhn *et al.*, A., 1938, II, 373, m.p. 89.5—90°, oxidised by Ba(MnO₄)₂ (4.4 O) in H₂O to 3-methoxy-2-methylpyridine-4:5-dicarboxylic acid (III), +H₂O, m.p. variable, ~209—210° (decomp.), and a small amount of a lactone (IV), C₈H₉O₃N, m.p. 108.5—109.5°. FeSO₄ gives no colour with (III) (absence of a 2-CO₂H in the C₅H₅N ring), and gives a phthalain with m-C₆H₄(OH)₂ [vicinal CO₂H, *i.e.*, CO₂H at positions 4 and 5]. The Na salt of (III) with Ca(OH)₂-N₂ at 360—370° gives 3-hydroxy-α-picoline (*picrate*, m.p. 147—148°), the nature of which is shown by absorption max. at 2400 and 3000 Å. at *pH* 10.5 (OH at C₃), its red FeCl₃ colour, its coupling with *p*-C₆H₄Br-N₂Cl, and its blue colour with 2:6-dichloroquinonechloroimide (absence of substituent *p*-to the OH).

II. The structure of -B₆ is proved by synthesis of the degradation products, (III) and (IV). CH₃Ac·CO·CH₂·OEt, CN·CH₂·CO·NH₂, and piperidine in 95% EtOH give 3-cyano-6-methyl-4-ethoxymethyl-2-pyridone, m.p. 210° (corr.), converted by conc. HCl or, better, 50% H₂SO₄ at 120° into the lactone, m.p. >320°, of 6-methyl-4-hydroxymethyl-2-pyridone-3-carboxylic acid. With HNO₃ (d 1.5) in H₂SO₄ this gives the 5-NO₂-lactone, m.p. 279—280° (decomp.), and thence successively (by POCl₃-PCl₅) the lactone, m.p. 176—178°, of 6-chloro-3-nitro-4-hydroxymethyl-α-picoline-5-carboxylic acid (V), (by H₂-PtO₂; 3 atm.; AcOH) the lactone, m.p. 280—282°, of 6-chloro-3-amino-4-hydroxymethyl-α-picoline-5-carboxylic acid, (by H₂-Pd-BaCO₃; abs. EtOH; 60°/3 atm.) the lactone, m.p. 224—226° (*picrate*, m.p. 229—230°), of 3-amino-4-hydroxymethyl-α-picoline-5-carboxylic acid [also obtained directly from (V) in EtOH-EtOAc], (by NaNO₂-25% H₂SO₄; boiling with more H₂SO₄) the lactone (VI), m.p. 272—273°, of 3-hydroxy-4-hydroxymethyl-α-picoline-5-carboxylic acid. The Me ether of (VI) is (IV); with Ba(MnO₄)₂ it gives (III). R. S. C.

Synthesis of vitamin-B₆. S. A. HARRIS and K. FOLKERS (J. Amer. Chem. Soc., 1939, 61, 1245—1247).—3-Cyano-6-methyl-4-ethoxymethyl-2-pyridone (cf. preceding abstract), fuming HNO₃, and a little CO(NH₂)₂ in Ac₂O give the 5-NO₂-derivative, m.p. 164—165°, converted by PCl₅-C₆H₆ into 6-chloro-

3-nitro-5-cyano-4-ethoxymethyl-α-picoline, m.p. 47—48°, and thence successively by H₂-Pt in EtOH at 3 atm. into 6-chloro-3-amino-5-cyano-4-ethoxymethyl-α-picoline, m.p. 146—148°, by H₂-PtO₂-Pd-C in AcOH at 3 atm. into 3-amino-5-aminomethyl-4-ethoxymethyl-α-picoline (*dipicrate*, m.p. 184—187°; *dihydrochloride*, m.p. 195°), by NaNO₂-2N-H₂SO₄ at 90° into 3-hydroxy-5-hydroxymethyl-4-ethoxymethyl-α-picoline (*hydrochloride*, m.p. 123—125°), by 48% HBr into 3-hydroxy-4:5-di(bromomethyl)-α-picoline hydrobromide, m.p. 223—224° (decomp. at 219°) (cf. Kuhn *et al.*, A., 1938, II, 373), and by hot H₂O, followed by AgCl, into 3-hydroxy-4:5-di(hydroxymethyl)-α-picoline (vitamin-B₆) hydrochloride. R. S. C.

Pyrrrolizidine (1-azadicyclo-[0.3.3]-octane). V. PRELOG and S. HEIMBACH (Ber., 1939, 72, [B], 1101—1103).—OEt·[CH₂]₃·Br and CHNa(CO₂Et)₂ in boiling abs. EtOH afford Et₂ γ-ethoxypropylmalonate, b.p. 145°/9 mm., converted by NaOEt and OEt·[CH₂]₃·Br into Et₂ α,γ-diethoxyheptane-δδ-dicarboxylate, b.p. 185°/8 mm., which is hydrolysed and decarboxylated to α,γ-diethoxyheptane-δ-carboxylic acid, b.p. 169°/0.08 mm. This is transformed by NaN₃ and conc. H₂SO₄ in presence of CHCl₃ at 50° into δ-amino-α,γ-diethoxyheptane, b.p. 132°/11 mm., which with 68% HBr at 100° yields α,γ-dibromo-δ-aminoheptane hydrobromide, m.p. 127—128°. Gradual addition of 0.1N-NaOH to this salt in H₂O at 50° followed by removal of any non-*tert.* base with PhSO₂Cl and NaOH leads to pyrrrolizidine (1-azadicyclo-[0.3.3]-octane), b.p. 148° (*picrate*, m.p. 257°; *picrolonate*, m.p. 227°; *platinichloride*, m.p. 205°). H. W.

New synthesis of norlupinane (1-azadicyclo-[0.4.4]-decane). V. PRELOG and K. BOŽIČEVIĆ (Ber., 1939, 72, [B], 1103—1106).—PhSO₃·[CH₂]₂·OEt and CHNa(CO₂Et)₂ yield Et₂ β-ethoxyethylmalonate, b.p. 152—156°/16 mm., hydrolysed and decarboxylated to OEt·[CH₂]₃·CO₂H, the Et ester of which is reduced by Na and EtOH to OEt·[CH₂]₄·OH. This is transformed by PBr₃ and C₅H₅N into δ-ethoxybutyl bromide (I), b.p. 69°/15 mm., which condenses with CHNa(CO₂Et)₂ to Et₂ δ-ethoxybutylmalonate (II), b.p. 158°/15 mm., hydrolysed and decarboxylated to ε-ethoxyhexoic acid, b.p. 147—148°/15 mm. (I) and (II) in presence of boiling NaOEt-EtOH give Et₂ α,δ-diethoxynonane-εε-dicarboxylate, b.p. 202—203°/14 mm., hydrolysed and decarboxylated to α,δ-diethoxynonane-ε-carboxylic acid, b.p. 169—170°/0.16 mm. The acid is converted by NaN₃ and conc. H₂SO₄ in presence of CHCl₃ at 50—55° into ε-amino-α,δ-diethoxynonane, b.p. 162°/15 mm., which is transformed by 69% HBr at 100° into α,δ-dibromo-ε-aminononane hydrobromide (corresponding *picrate*, m.p. 118—119°). The salt is transformed by 0.1N-NaOH exclusively into norlupinane A, b.p. 69—70°/11 mm., further identified as the *picrate*, m.p. 196°, *picrolonate*, m.p. 249°, *aurichloride*, m.p. 167—168°, and *platinichloride*, m.p. 333° (decomp.). H. W.

Reaction of chloronitrobenzenes with unilaterally positivised ethylenes. R. WIZINGER and M. L. COENEN (J. pr. Chem., 1939, [ii], 153, 127—159).—It is shown that an ethylene through strong positivisation of C₆₀ can develop a very marked proton affinity at C₆, and hence like the typical

$C_6H_4 \begin{smallmatrix} \text{CMe}_2 \\ \text{NMe} \end{smallmatrix} C: CMe_2$ does not yield a primary adduct with (I). 1 : 2 : 4- $C_6H_3Cl(NO_2)_2$ is less reactive than (I) but in boiling C_6H_6 at greater concn. unites with very strongly positivised ethylenes to the following : 1-methyl-2-2' : 4'-dinitrophenylmethylen-1' : 2-di-hydroquinoline, decomp. 210—212°; 5-methoxy-2-dinitrophenylmethylen-1 : 3 : 3-trimethylindoline, m.p. 148°; 2-dinitrophenylmethylen-1 : 3 : 3-trimethylindoline, m.p. 139—140°. 4 : 6-Diphenyl-2-methylene-pyran and 10-methyl-5-methylenedihydroacridine give characteristic colours but not pure products; reaction is not observed with $(NMe_2 \cdot C_6H_4)_2 C:CH_2$ and only a colour with $(NEt_2 \cdot C_6H_4)_2 C:CH_2$. Reactions with *o*- or *p*- $C_6H_4Cl \cdot NO_2$ have not been observed 1 : 2 : 4- $C_{10}H_5Cl(NO_2)_2$ yields 5-methoxy-1 : 3 : 3-trimethyl-2-2' : 4'-dinitro-1'-naphthylmethylenindoline, m.p. 174°, 1 : 3 : 3-trimethyl-2-2' : 4'-dinitro-1'-naphthylmethylenindoline, decomp. ~220°; α -tetraethyl-diaminodiphenyl- β -2 : 4-dinitro-1-naphthylethylene, m.p. 211°, and α -tetramethyldiaminodiphenyl- β -2 : 4-dinitro-1-naphthylethylene, decomp. 238—240°. 1 : 3 : 4 : 6- $C_6H_2Cl_2(NO_2)_2$ affords 5-methoxy-1 : 3 : 3-trimethyl-2-3'-chloro-4' : 6'-dinitrophenylmethylenindoline, m.p. 129—130°, 1 : 3 : 3-trimethyl-2-3'-chloro-4' : 6'-dinitrophenylmethylenindoline, m.p. 187—188°, and α -tetraethyl-diaminodiphenyl- β -3'-chloro-4' : 6'-dinitrophenylethylene, m.p. 153—154°. 1 : 2 : 3 : 4 : 6- $C_6HCl_3(NO_2)_2$ gives 5-methoxy-1 : 3 : 3-trimethyl-2-2' : 3'-dichloro-4' : 6'-dinitrophenylmethylenindoline,

Compounds of zinc salts with quinoline.—See A., 1939, I, 380.

Nitrogen compounds from petroleum distillates. XII. Fractional sulphiting of bases and fractional degassing of their hydrogen sulphites. S. M. ROBERTS and J. R. BAILEY. XIII. Isolation of four quinoline homologues and two aromatic bases of probable trinuclear cyclic structure. W. N. AXE and J. R. BAILEY (J. Amer. Chem. Soc., 1938, **60**, 3025—3028, 3028—3032; cf. A., 1938, II, 245).—XII. Fractional formation and thermal decomp. of the H sulphites of bases from kerosene are described. Bases, otherwise inseparable, are thus separated. Unless "degassing," i.e., the decomp. of the salts by heating in vac., is effected in N_2 or CO_2 etc., some oxidation to sulphates occurs.

XIII. The fractionation described above depends on the ionisation consts. of the bases. The fraction,

b.p. about 295°, of bases from kerosene yields by the more usual methods *bases*, (I) $C_{13}H_{15}N$ and (II) $C_{14}H_{17}N$. The sulphite procedure yields 2:3-dimethyl-8-n-propylquinoline (III), m.p. 14.5–15.5°, b.p. 299.5° [different from (II)]; *nitrate*, m.p. 169° (decomp.); *picrate*, m.p. 198–199°; *H sulphate*, m.p. 212–212.5°; *hydrochloride*, m.p. 161–162°; $ZnCl_2$ double salt, m.p. 193–194°, oxidised by $K_2Cr_2O_7-H_2SO_4$ to 2:3-dimethylquinoline-8-carboxylic acid, m.p. 201–202° (with soda-lime yields 2:3-dimethylquinoline), and synthesised by the reactions: $CH_3Ph \cdot MgCl + Me_2SO_4 \rightarrow PhPr^a \rightarrow (40^\circ) 1:2:4-C_6H_3Pr^a(NO_2)_2 \rightarrow [+(NH_4)_2S] 2:1:4-NO_2 \cdot C_6H_3Pr^a \cdot NH_2 \rightarrow o-C_6H_4Pr^a \cdot NO_2 \rightarrow (H_2-Ni) o-C_6H_4Pr^a \cdot NH_2$ (IV); (IV) + $CHMe \cdot CMe \cdot CHO$ (+hot, conc. HCl) \rightarrow (III). The undecomposed residue contains [as *H sulphate*, m.p. 298° (decomp.)] 2:3:4:8-tetramethylquinoline, m.p. 77–78° [different from (I)]; *picrate*, m.p. 240° (decomp.); *hydrochloride*, m.p. 252–253° (decomp.); *nitrate*, m.p. 184.5° (decomp.); *zincichloride*, m.p. 266–267°; *phthalone*, m.p. 264°, oxidised to 2:3:4-trimethylquinoline-8-carboxylic acid, m.p. 233.5–234° (with soda-lime at $\geq 360^\circ$ gives 2:3:4-trimethylquinoline), and synthesised from $o-C_6H_4Me \cdot NH_2$, $CHMeAc_2$, and conc. HCl. The bases, b.p. 340°, from transformer oil yield, by way of the picrates and *H sulphates*, a *base*, $C_{15}H_{13}N$, m.p. 83.5–84° [*picrate*, m.p. 228.5–229.5°; *H sulphate*, m.p. 265–267° (decomp.)], and then by the sulphite procedure a *base*, $C_{16}H_{15}N$, m.p. 86–87° [*picrate*, m.p. 338–339°; *nitrate*]; these bases are probably acridines or naphthoquinolines. R. S. C.

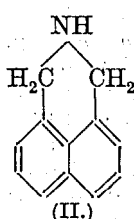
Nitrogen compounds in petroleum distillates. XIV. Isolation of 2:4-dimethyl-8-ethylquinoline from the kerosene distillate of California petroleum. W. N. AXE (J. Amer. Chem. Soc., 1939, 61, 1017–1019).—2:4-Dimethyl-8-ethyl- (I) and -8-n-propylquinoline are isolated from California petroleum. Common quinoline bases isolated from petroleum are alkylated in positions 2, 3, and 8, those alkylated in positions 2, 4, and 8 being rare. (I), b.p. 288°/747 mm. (*picrate*, m.p. 165–166°; *zincichloride*, m.p. 261–262°), and $K_2Cr_2O_7-H_2SO_4-H_2O$ give 2:4-dimethylquinoline-8-carboxylic acid, m.p. 241–242° (decomp.), also obtained from 2:4:8-trimethylquinoline. $o-C_6H_4Et \cdot NH_2$ (modified purification) and CH_2Ac_2 at 100° yield (I). R. S. C.

Mechanisation of decarboxylation. II. Production of cyanide-like ions from α -picolinic, quinaldinic, and isoquinaldinic acids. M. R. F. ASHWORTH, R. P. DAFFERN, and D. L. HAMMICK (J.C.S., 1939, 809–812).—When the above acids are decarboxylated in the presence of aldehydes and ketones, carbinols containing the pyridyl, quinolyl, and isoquinolyl radicals are obtained. This reaction is sp. for these acids and it is suggested that the reason for this is that the anion radicals produced when the acids lose CO_2 contain $[N=C]^-$, which when added to CO would be analogous to cyanohydrin formation. Chelation between the acidic and basic centres is suggested to explain the readiness with which α -imino-carboxylic acids lose CO_2 and the action of carboxylase. The following are described: *diphenyl-2-quinolyl*, m.p. 189°, *phenyl-2-pyridyl*-

(*phenylurethane*, m.p. 143.5°), *phenyl-2-pyridylmethyl*- (*picrate*, m.p. 176°; *phenylurethane*, m.p. 151°), *diphenyl-2-pyridyl*, and *p-methoxyphenyl-2-pyridylcarbinol*, m.p. 131.5° (*phenylurethane*, m.p. 145°).

F. R. S.

Electro-reduction of naphthalimide. E. SPÄTH, F. KUFFNER, and F. KITTEL (Ber., 1939, 72, [B], 1109–1112; cf. A., 1929, 194).—Electrolytic reduction of naphthalimide (I) at a Pb



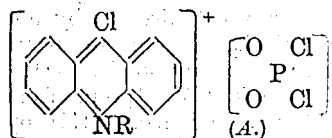
cathode gives 1:2:3:6-tetrahydro-naphthalino-1':9':8'-3:4:5-pyridine (II), m.p. 102–103° (vac.) (*p-nitrobenzoyl* derivative, m.p. 171.5°), oxidised by $KMnO_4$ in acid solution to (I). This is converted by Pd sponge at 200° into 4:5-trimethyleneisoquinoline, m.p. 47.5–48° (*picrate*, m.p. 228–230°), which does not react with $p-NO_2 \cdot C_6H_4 \cdot COCl$ and gives a *methiodide*, m.p. 204–205° (vac.), oxidised by alkaline $K_3Fe(CN)_6$ to 2-methylisoquinoline, m.p. 105–106°; it gives a characteristic additive product, m.p. 134–135° (vac.), with $HICl_2$. H. W.

Bromination of some 4-quinolones. H. P. W. HUGGILL and S. G. P. PLANT (J.C.S., 1939, 784–787).—1:2:3:4-Tetrahydroacridone (I) and Br (1 mol.) give 7-bromotetrahydroacridone, also obtained from 5-bromoanthranilic acid and cyclohexanone, and converted ($POCl_3-PCl_5$) into 5-chloro-7-bromotetrahydroacridine, m.p. 99°; the bromination also yields other products containing reactive Br, from which a compound, m.p. 152°, can be prepared by the action of $POCl_3-PCl_5$. Further bromination of (I) affords 7:9-dibromotetrahydroacridone, m.p. 287° (also obtained from 3:5-dibromoanthranilic acid), which with $POCl_3-PCl_5$ gives 5-chloro-7:9-dibromotetrahydroacridine, m.p. 170–173°. 7:9-Dimethyltetrahydroacridone, converted ($POCl_3-PCl_5$) into 5-chloro-7:9-dimethyltetrahydroacridine, m.p. 94°, is brominated to a Br-derivative, m.p. 196° (decomp.), which gives a pyridinium salt, and suggests that the Br is attached to the reduced ring. 2:6:8-Trimethyl-4-quinolone yields a Br-derivative, m.p. 272–274°, unchanged by C_5H_5N , and forming 4-chloro-2-bromo-2:6:8-trimethylquinoline, m.p. 107°. 1:3:4- $C_6H_3Me_2 \cdot NH_2$ and $CH_2Ac \cdot CO_2Et$, followed by MeI, give 2:3:6:8-tetramethyl-4-quinolone, m.p. 300°, converted into 4-chloro-2:3:6:8-tetramethylquinoline, m.p. 89°. Anthranilic acid with 1-keto-1:2:3:4-tetrahydrocarbazole, and cyclohexane-1:2-dione and -1:4-dione affords respectively 5-keto-5:6:7:10-tetrahydroacridindoline, m.p. $>360^\circ$, N-2'-ketocyclohexylideneanthranilic acid, m.p. 172°, and the di-o-carboxyanil of cyclohexane-1:4-dione, m.p. 261° (decomp.). F. R. S.

Acridine. XXI. Quaternary 10-methoxyacridinium bases. K. LEHMSTEDT and F. DOSTAL (Ber., 1939, 72, [B], 1071–1074).—10-Methoxyacridone is converted by LiPh in C_6H_6 followed by H_2O into 5-hydroxy-10-methoxy-5-phenyl-5:10-dihydroacridine (I), decomp. 141–142°, which passes at $\sim 250^\circ$ into CH_2O and 5-phenylacridine. (I) is converted by crystallisation from MeOH into 5:10-dimethoxy-5-phenyl-5:10-dihydroacridine, decomp. 150–151°.

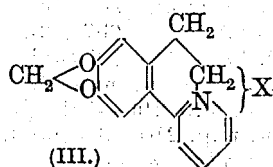
When the solution of (I) in HCl is treated with NH_3 , 5-amino-10-methoxy-5-phenyl-5:10-dihydroacridine, decomp. 116—117.5°, is pptd.; this is transformed by boiling EtOH into 10-methoxy-5-ethoxy-5-phenyl-5:10-dihydroacridine, m.p. 180.5—181.5° (decomp.), also obtained from (I) and boiling EtOH. Prolonged boiling of (I) with 2N-HCl followed by pptn. with KOH gives 5-phenylacridine 10-oxide, decomp. 228—230°, and 5-amino-5-hydroxy-10-methoxy-5:10-dihydroacridine, decomp. 115—117°. H. W.

Action of phosphoryl chloride and oxalyl chloride on acridones. K. GLEU, S. NITZSCHE, and A. SCHUBERT (Ber., 1939, 72, [B], 1093—1099).—N-Arylanthranilic acids are transformed by POCl_3 into acridones, converted by further action of the reagent into 5-chloroacridones. The formation of the last-named is preceded by that of additive compounds (1:1) of acridone and POCl_3 (the parent compound, its 2-Me, 10-Me, and 10-Ph derivatives are described). The structure A is assigned to these compounds since they have salt-like character, being readily sol. in cold H_2O



but insol. in org. media; those without substituent at (10) are quantitatively hydrolysed to the 5-chloroacridones whilst those with such substituent are essentially similar in behaviour but can yield only 10-substituted acridones. Analogy is traced between $\text{H}(\text{PO}_3\text{Cl}_2)$ and HClO_4 . The supposed acridone dichlorides obtained by the action of $\text{POCl}_3 + \text{PCl}_5$ on 10-substituted acridones are compounds of structure (A). For the prep. of the dichlorides PCl_5 is unsuitable since POCl_3 is a product of the change. Acridones are transformed by oxalyl chloride (free from HCl) in hot xylene into acridone dichlorides (10-Me and 10-Ph compounds described); evidence of the formation of an intermediate, additive compound is not obtained, probably owing to the instability of the anion $[\text{O}_2\text{C}\cdot\text{COCl}]^-$ which immediately decomposes into $\text{CO} + \text{CO}_2 + \text{Cl}^-$. H. W.

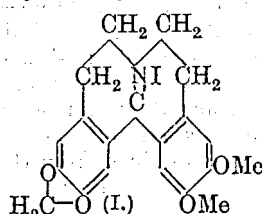
Synthesis of hetero-rings containing nitrogen. XV. Oxidation of β -phenylethyl-pyridinium and -quinolinium salts. S. SUGASAWA and N. SUGIMOTO (Ber., 1939, 72, [B], 977—979).—1- β -Phenylethylpyridinium bromide is oxidised to 1- β -phenylethylpyrid-2-one, m.p. 87°. Oxidation of 1- β -3':4'-dimethoxyphenylethylpyridinium bromide could not be effected with $\text{K}_3\text{Fe}(\text{CN})_6$ in presence of aq. NH_3 , Na_2CO_3 , Na_3PO_4 , or NaOAc , with Ag_2O or KMnO_4 , or in presence of C_6H_6 . 1- β -3':4'-Methylenedioxyphenylethylpyrid-2-one (I), m.p. 148°, 1- β -4'-methoxyphenylethylquinol-2-one, m.p. 110.5°, and 1- β -3':4'-methylenedioxyphenylethylquinol-2-one (II), m.p. 138°, are described. Only brown products insol. in C_6H_6



are given by 6:7-dimethoxy-1- β -3':4'-dimethoxyphenylethylquinolinium bromide. Successive treatments of (I) with POCl_3 in xylene at 135—140° and HI lead to 4':5'-methylenedioxy-9:10-dehydro-3:4-dihydro-1':2'-1:2-benzoquinolizinium

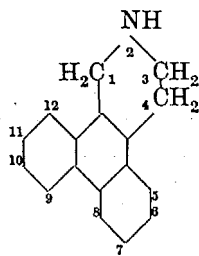
iodide [(III); X = I], m.p.: 191°, hydrogenated (Adams) to a non-cryst. base, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}$ [hydriodide, m.p. 198°; hydrochloride, m.p. 213°; methiodide, m.p. 164° (slight decomp.)]. Similarly, (II) is transformed into 4':5'-methylenedioxy-9:10-dehydro-3:4-dihydro-1':2'-1:2-1':2'-5:6-dibenzoquinolizinium iodide, m.p. 254° (decomp.). The corresponding hydrogenated base and its derivatives are not cryst.; the very hygroscopic hydrochloride has m.p. ~227°. H. W.

Syntheses of hetero-rings containing nitrogen. XVI. Syntheses of dibenzoquinolizine derivatives. II. Synthesis of 4':5'-dimethoxy-4'':5''-methylenedioxy-3:4:5:6-tetrahydro-1':2'-1:2-1':2'-7:8-dibenzoquinolizine and the corresponding tetramethoxy-compound. S. SUGASAWA and K. KAKEMI (Ber., 1939, 72, [B], 980—984).—Oxidation of 6:7-dimethoxy-3:4-dihydroisoquinoline methiodide with aq. $\text{K}_3\text{Fe}(\text{CN})_6$ gives 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinol-1-one, m.p. 125—126°. 6:7-Dimethoxy-3:4-dihydroisoquinoline and β -3:4-methylenedioxyphenylethyl bromide give 6:7-dimethoxy-2- β -3':4'-methylenedioxyphenylethyl-3:4-dihydroisoquinolinium bromide, m.p. 187—188°, converted by oxidation with $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution in presence of C_6H_6 , followed by treatment with POCl_3 at 100° and then with NaI, into 4':5'-dimethoxy-4'':5''-methylenedioxy-9:10-dehydro-3:4:5:6-tetrahydro-1':2'-1:2-1':2'-7:8-dibenzoquinolizinium iodide (I), m.p. 188—189°, the corresponding chloride, m.p. 150°, is reduced to 4:5'-dimethoxy-4'':5''-methylenedioxy-3:4:5:6-tetrahydro-1':2'-1:2-1':2'-7:8-dibenzoquinolizine (+0.5EtOH), m.p. 101—102° [hydrochloride (+EtOH), m.p. 219—220°; hydriodide, m.p. 209° (decomp.); methiodide, m.p. 199—200°; picrate, decomp. 176—177°]; the free base is dehydrogenated by I to (I). Similarly, 6:7-dimethoxy-2- β -3':4'-dimethoxyphenylethyl-3:4-dihydroisoquinolinium bromide, m.p. 192°, is converted into 4':5':4'':5''-tetramethoxy-9:10-dehydro-3:4:5:6-tetrahydro-1':2'-1:2-1':2'-7:8-dibenzoquinolizinium iodide (+0.5H₂O), m.p. 195°, and thence into 4':5':4'':5''-tetramethoxy-3:4:5:6-tetrahydro-1':2'-1:2-1':2'-7:8-dibenzoquinolizine, m.p. 116° [hydrochloride (+0.5EtOH), m.p. 236—237°; hydriodide, m.p. 207°]. H. W.

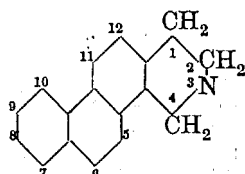


Phenanthrene series. XXII. Derivatives of dibenzisoquinoline and naphthisoquinoline. E. MOSSETTIG and (Miss) E. L. MAY (J. Amer. Chem. Soc., 1938, 60, 2962—2966; cf. A., 1938, II, 510).—The appropriate phenanthraldehyde, MeNO_2 , and KOH-EtOH give 9- (I), m.p. 173—173.5° (corr.), 3- (II), m.p. 180—180.5° (corr.), and 2- β -nitrovinylphenanthrene, m.p. 134.5—137° (corr.), reduced electrolytically to 9-, m.p. 307—309° (decomp.) (CHO-derivative, m.p. 111—112°), 3- (III), m.p. 254—256° [CHO-derivative, m.p. 122—124° (corr.)], and 2- β -aminoethylphenanthrene, m.p. 317—318° (picrate, m.p. 225—226°). 40% aq. CH_2O converts the amines into 1:2:3:4-tetrahydrodibenz[f,h]isoquinoline (IV), m.p. 223—225° [hydrochloride, m.p. 304—306° (de-

comp.), and (?) 1:2:3:4-tetrahydronaphth[1:2-h]isoquinoline (V) [hydrochloride, m.p. 313—315° (decomp.)], but (III) was unchanged by CH_2O . With NaOMe-MeOH (I) and (II) give 9-, m.p. 134—134.5°



(IV.)



(V.)

(corr.), and 3- β -nitro- α -methoxyethylphenanthrene, m.p. 102—104°, hydrogenated (PtO_2) in EtOH to 9-, m.p. 252—253° (decomp.) [picrate, m.p. 215—217° (decomp.)]; CHO- , m.p. 138—140° (corr.), and Bz derivative, m.p. 147.5—148.5° (corr.), and 3- β -amino- α -ethoxyethylphenanthrene [hydrochloride, m.p. 232—233° (decomp.)], which resisted cyclisation by all methods, as also do all the CHO- derivatives. With MeI-KOH in COMe_2 (IV) gives the methiodide, m.p. 268—270°, of its 2-Me derivative, and thence at 200—220°/high vac. the 2-Me derivative, m.p. 113.5—114° (corr.) (hydrochloride, cryst.). (V) gives similarly 3-methyl-1:2:3:4-tetrahydronaphth[1:2-h]isoquinoline [hydrochloride, m.p. 257—259° (decomp.)]; methiodide, m.p. 244.5—246° (decomp.)], and, in some experiments, 2- β -dimethylaminoethylphenanthrene hydrochloride, m.p. 247—249°, also obtained from the $\text{NH}_2[\text{CH}_2]_2$ compound. R. S. C.

Synthesis of coloured derivatives of nirvanol.

J. J. SPURLOCK with H. R. HENZE (J. Amer. Chem. Soc., 1938, 60, 3005—3007).—5-Phenyl-5-ethylhydantoin is nitrated and then hydrogenated, but the isomerides produced resist separation. $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-COEt}$, m.p. 99—100°, KCN , and $(\text{NH}_4)_2\text{CO}_3$ in EtOH give 5-m-nitrophenyl-5-ethylhydantoin, m.p. 219—220°, reduced ($\text{H}_2\text{-PtO}_2$) in COMe_2 to the NH_2 -compound, $+\text{H}_2\text{O}$, double m.p. 82—83° and 165—166°, which is diazotised and coupled with $\beta\text{-C}_{10}\text{H}_7\text{-OH}$, $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$, NPhMe_2 , and G salt, yielding dyes, m.p. 276—277° (decomp.), 247—248°, 233—235°, and a Ba salt, $+\text{8H}_2\text{O}$, respectively. M.p. are corr. R. S. C.

5-Alkyl-5-crotylbarbituric acids. W. J. DORAN and H. A. SHONLE (J. Amer. Chem. Soc., 1938, 60, 2880—2882).—The following are prepared: 5-ethyl- (? cis-trans-isomerides), m.p. 108—110° and 120—121°, -n-propyl-, m.p. 160—161°, -isopropyl-, m.p. 144—145° (lit., 137—138°), -n-, m.p. 142—143°, -sec-, m.p. 130—131°, and -iso-butyl-, m.p. 126—127° (lit., 115°), - α -methyl-n-butyl-, m.p. (anhyd.) 110—113° and $(+\text{H}_2\text{O})$ 88—90°, and -isoamyl-, m.p. 147—148°, -5-crotylbarbituric acid, which have a very short anaesthetic effect. 5-Ethyl-5- α -methylallylbarbituric acid, m.p. 146.5—148°, has a slightly longer effect. 5-n-Butyl-5-crotylthiolbarbituric acid, m.p. 238—239°, is only convulsant. R. S. C.

Phenyl alkyl nitrogen substitution. Reactivity in the barbituric acid series. D. NIGHTINGALE

and R. G. TAYLOR (J. Amer. Chem. Soc., 1939, 61, 1015—1017).—5:5-Dibromo-1-phenyl-3-methyl- (I) and -3-n-butyl-barbituric acid (II) resemble the 1:3- Ph_2 derivatives in not reacting with amines, $\text{CS}(\text{NH}_2)_2$, or KSCN . $\text{CH}_2(\text{CO}_2\text{H})_2$ with N-phenyl-N'-n-butyl-carbamide (prep. from PhNCO and NH_2Bu^n in dry Et_2O), m.p. 135°, NHPh-CO-NHMe , or $o\text{-C}_6\text{H}_4\text{Me-NH-CO-NH}_2$ in Ac_2O gives (II), m.p. 96—98° (5-anilinomethylene, m.p. 146—148°, and 5:5- Br_2 -derivative, m.p. 108—110°), (I) (5-anilinomethylene, m.p. 170°, and 5:5- Br_2 -derivative, m.p. 161°), and 1-o-tolylbarbituric acid, m.p. 181°. 5:5-Dibromo-1:3-di-o-tolylbarbituric acid melts at 190—191°. R. S. C.

Pyrimidines. CLIX. Synthesis of 6- and 5-benzyluracils. T. B. JOHNSON and J. C. AMBELANG (J. Amer. Chem. Soc., 1938, 60, 2941—2944; cf. A., 1938, II, 379).— $\text{CH}_2\text{Ph-CO-CH}_2\text{-CO}_2\text{Et}$ (I) and $\text{CS}(\text{NH}_2)_2$ with a little HCl give (?) the ureide, converted by hot KOH-EtOH into 2-thio-6-benzyluracil (II), m.p. 222—223°, also obtained directly by hot NaOEt-EtOH . $\text{NH}_2\text{C(SET)-NH}_2$ (I), and aq. KOH give 4-hydroxy-2-ethylthiol-6-benzylpyrimidine (III), m.p. 128—129°. 6-Benzyluracil (IV) [prep. from (II) by 10% aq. $\text{CH}_2\text{Cl-CO}_2\text{H}$ and from (III) by HCl], m.p. 261—262°, with Br-AcOH at 40—50° gives the 5-Br-derivative (V), m.p. 230—232° (gives BzOH by KMnO_4), and with $\text{Cl}_2\text{-MeOH}$ gives 5:5-dichloro-2:4-diketo-6-methoxy-6-benzylhexahydropyrimidine, m.p. 157—159° (decomp.) (160—162°), unchanged by $\text{C}_5\text{H}_5\text{N}$, but converted by HBr-AcOH into 5-chloro-6-benzyluracil, m.p. 266—267°, which is also obtained in poor yield from (IV) and Cl_2 in 10% AcOH . Attempts to cyclise (V) by AlCl_3 failed. $\text{Ph-[CH}_2\text{]}_2\text{-CO}_2\text{Et}$ (prep. by $\text{H}_2\text{-Raney Ni}$) and HCO_2Et with Na in Et_2O give the HCO- derivative, the Na salt of which with $\text{CS}(\text{NH}_2)_2$ in EtOH gives 2-thio-5-benzyluracil, m.p. 210—211°. With 10% $\text{CH}_2\text{Cl-CO}_2\text{H}$ this yields 5-benzyluracil (VI), m.p. 294—295°, converted by $\text{Cl}_2\text{-MeOH}$ into 5-chloro-2:4-diketo-6-methoxy-5-benzylhexahydropyrimidine, double m.p. 217—218° and 232—234° [converted by HBr-AcOH into (VI)]. R. S. C.

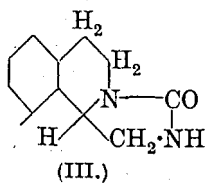
Preparation of L-tartaric acid from racemic tartaric acid through resolution by a substituted benzimidazole base. W. T. HASKINS and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1266—1268).—Aldonic acids or their lactones with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and 1—2 mols. of HCl in hot H_2O give (usually) 52—75% yields of 2-substituted benzimidazoles. Thus are obtained 2-D-glucido-D-gulo- (I), m.p. 215° (decomp.), $[\alpha] +14.3^\circ$, 2-D-glucido-D-ido-, m.p. 192° (decomp.), $[\alpha] -27.6^\circ$, 2-D-manno-D-gala-, m.p. 241° (decomp.), $[\alpha] +49.5^\circ$, and 2-D-gala-L-manno-, m.p. 218° (decomp.), $[\alpha] +18.5^\circ$, -hexahydroxyhexyl-benzimidazole, 2-D-glucido-, m.p. 210° (decomp.), $[\alpha] +8.9^\circ$, 2-D-gulo-, m.p. 201° (decomp.), $[\alpha] +16.7^\circ$, 2-D-manno-, m.p. 224° (decomp.), $[\alpha] -23.7^\circ$, 2-D-galacto-, m.p. 246° (decomp.), $[\alpha] +44.4^\circ$, 2-D-ido-, m.p. 154—156°, $[\alpha] -19.2^\circ$, 2-D-altro-, m.p. 198° (decomp.), $[\alpha] -48.1^\circ$, 2-D-talo-, m.p. 190—191°, $[\alpha] -23.0^\circ$, and L-mannomethylo-, m.p. 210° (decomp.), $[\alpha] +29.1^\circ$, -pentahydroxy-n-amylobenzimidazole. $[\alpha]$ are $[\alpha]_D^{20}$ in 0.1N-HCl. L-(—) is very readily obtained

from *dl*-tartaric acid by means of its salt, $+2\text{H}_2\text{O}$ (lost at $78^\circ/\text{vac.}$), m.p. $118\text{--}125^\circ$, $[\alpha]_{\text{D}} -0.5^\circ$ in H_2O . M.p. are corr. R. S. C.

Chemiluminescent organic compounds. VII. Substituted phthalaz-1:4-diones. Effect of substituents on the luminescent power. H. D. K. DREW and R. F. GARWOOD (J.C.S., 1939, 836—837).—Observations on new diones tend to confirm the conclusion previously reached (cf. Drew *et al.*, A., 1937, II, 118). In the halogenated diones, the lighter is the halogen the more its presence enhances the luminescent power. 3-Bromophthalimide, m.p. 260° , prepared from the corresponding NH_2 -compound, with N_2H_4 gives 5-bromophthalaz-1:4-dione, m.p. 322° . 6-Bromo-, m.p. 343° , and 6-iodo-phthalaz-1:4-dione, m.p. 345° , are similarly prepared. The following are prepared from N_2H_4 and the appropriate anhydride: 5-methylphthalaz- (I), m.p. 340° , $\beta\beta$ -naphthalaz-, m.p. 345° [Na salt ($+\text{H}_2\text{O}$)], 6-nitro- $\beta\beta$ -naphthalaz-, m.p. $>350^\circ$ [Na salt ($+\text{H}_2\text{O}$)], 6-amino- $\beta\beta$ -naphthalaz-, m.p. 320° (decomp.), and $\alpha\beta$ -naphthalaz-1:4-dione, m.p. $>360^\circ$. (I) shows a lower luminescent power than phthalazdione and this effect is anomalous.

F. R. S.

Catalytic hydrogenation of 1-cyano-2-benzoyl-1:2-dihydroisoquinoline (Reissert's substance from isoquinoline). H. RUFÉ and W. FREY (Helv. Chim. Acta, 1939, 22, 673—683).—Addition of BzCl to a suspension of isoquinoline in 10% aq. KCN gives 1-cyano-2-benzoyl-1:2-dihydroisoquinoline, m.p. 128° (Reissert's substance from isoquinoline), reduced (Ni-EtOAc) by H_2 at $90^\circ/70$ atm. to 1-benzamidomethyl-1:2:3:4-tetrahydroisoquinoline (I), m.p. 125° (NO-derivative, m.p. 127° , reduced by Zn dust in AcOH-EtOH to the hydrazino-compound, m.p. 141° , in poor yield; *Bz*, m.p. 144° , and *Ac*, m.p. 201° , derivatives). This is slowly hydrolysed by boiling 20% HCl to 1-aminomethyl-1:2:3:4-tetrahydroisoquinoline (II), b.p. $153^\circ/12$ mm. [hydrochloride ($+2\text{H}_2\text{O}$), decomp. 281° ; perchlorate, m.p. 117° ; picrate, m.p. 186° ; citrate ($+2\text{H}_2\text{O}$), m.p. 166° ; oxalate, decomp. 198° ; tartrate, m.p. 125° ; phenylthiocarbamide derivative, $\text{C}_{24}\text{H}_{24}\text{N}_4\text{S}_2$, m.p. 188° ; carbamide compound, $\text{C}_{11}\text{H}_{15}\text{ON}_3$, m.p. 173° ; *Ac*₂ derivative]. ClCO_2Et and (II) in Et_2O afford 1-carbethoxyaminomethyl-1:2:3:4-tetrahydroisoquinoline, b.p. $166^\circ/12$ mm., and the iminazolone (III), m.p. 148° , also obtained readily by use of COCl_2 ; in the presence of $\text{C}_6\text{H}_5\text{N}$ at room temp. the product is *Et* 1-carbethoxyamino-1:2:3:4-tetrahydroisoquinoline-2-carboxylate, b.p. $180^\circ/12$ mm., m.p. 103° . (I) is trans-



formed by MeI in MeOH at 100° into (?) 2-methyl-1-benzamidomethyl-1:2:3:4-tetrahydroisoquinoline methiodide, m.p. 152° , which loses MeI when hydrolysis is attempted. With boiling MeI-MeOH (I) yields 2-methyl-1-benzamidomethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 122° , hydrolysed to 2-methyl-1-aminomethyl-1:2:3:4-tetrahydroisoquinoline (IV), b.p. $143.5^\circ/12$ mm. (hydrochloride, m.p. 256° ; picrate, m.p. 192°). (II) is converted by MeI and KOH in boiling MeOH into 2-methyl-1-dimethylaminomethyl-

1:2:3:4-tetrahydroisoquinoline methiodide, m.p. 199° (IV), and 2-methyl-1-dimethylaminomethyl-1:2:3:4-tetrahydroisoquinoline, b.p. $135^\circ/12$ mm. (picrate, m.p. 202°). Similar results are obtained when methylation is effected under pressure.

H. W.

Heterocyclic compounds containing nitrogen.

XLII. Linear and angular benzodipyridines.

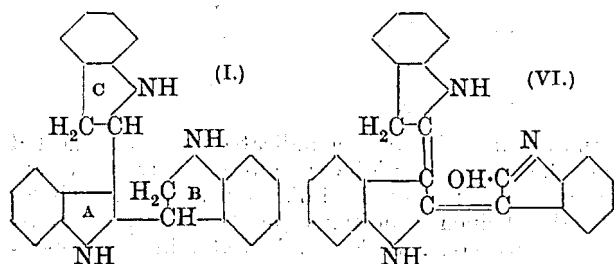
VI. 1:5-Anthrazoline and 4:5-phenanthroline. P. RUGGLI and E. PREISWERK (Helv. Chim. Acta, 1939, 22, 478—495; cf. A., 1939, II, 231).—The



name anthrazoline and the indicated nos. are suggested for the benzodipyridines; alternatively they are designated 1:8- or 1:5-diaza-anthracene. Under strictly defined conditions $p\text{-C}_6\text{H}_4(\text{CHO})_2$ is transformed by conc. H_2SO_4 and KNO_3 into nitroterephthalaldehyde (I), m.p. 97° (lit. m.p. 86°) [dioxime, m.p. $175\text{--}176^\circ$; diphenylhydrazone, m.p. 200° (decomp.) after softening at 185° ; dianil, m.p. $133\text{--}134^\circ$], which when reduced chemically or catalytically gives higher condensation products which could not be divided or acetylated. $\text{CH}_2(\text{CO}_2\text{H})_2$ and (I) are condensed in $\text{C}_6\text{H}_5\text{N}$ at $40\text{--}50^\circ$ and then at 90° to nitro-p-phenylenediacrylic acid (II), decomp. $300\text{--}305^\circ$ after becoming discoloured at $\sim 290^\circ$, transformed by the successive action of PCl_5 and the requisite alcohol into the *Me*₂, m.p. 166° , *Et*₂, m.p. 125° , and *diamyl*, m.p. $93\text{--}94^\circ$, ester. Hydrogenation (Raney Ni in $\text{EtOH-MeOH-EtOAc-H}_2\text{O}$) of (II) at room temp. affords amino-p-phenylenediacrylic acid, softens at 360° (decomp.) after becoming discoloured at 280° [*Ac*₂ derivative, softens at $\sim 310\text{--}315^\circ$ (decomp.) after darkening at $\sim 310\text{--}315^\circ$; *Me*₂ ester, m.p. 159° , and its *Ac* derivative, m.p. 168° ; *Et*₂ ester, m.p. 178°]. This is converted by boiling conc. HCl into 2-keto-1:2-dihydroquinoline-7-acrylic acid (III), which becomes brown at $330\text{--}335^\circ$ (*Et* ester, m.p. $209\text{--}210^\circ$), converted by the successive action of PCl_5 and MeOH into *Me* 2-methoxyquinoline-7-acrylate, m.p. $193\text{--}195^\circ$. Hydrogenation (Raney Ni in $\text{MeOH-EtOH-EtOAc-H}_2\text{O}$) of (III) 75° leads to 2-keto-1:2:3:4-tetrahydroquinoline-7-propionic acid (IV), m.p. 240° (*Me*, m.p. $142\text{--}143^\circ$, and *Et*, m.p. $123\text{--}124^\circ$, ester). Conc. H_2SO_4 , KNO_3 , and (III) at room temp. afford 6-nitro-2-keto-1:2-dihydroquinoline-7-acrylic acid, slow decomp. 310° . Nitration of (IV) gives 6-nitro-2-keto-1:2:3:4-tetrahydroquinoline-7-propionic acid (V), m.p. 260° (*Et* ester, m.p. $137\text{--}138^\circ$), or, if treatment is prolonged, 6:8-dinitro-2-keto-1:2:3:4-tetrahydroquinoline-7-propionic acid (VI), m.p. $234\text{--}235^\circ$ (decomp.) (*Me* ester, m.p. 166°). Hydrogenation (Raney Ni in $\text{EtOAc-EtOH-MeOH-H}_2\text{O}$) of (V) at room temp. leads to 2:6-diketo-octahydro-1:5-anthrazoline (VII), darkens at $\sim 360^\circ$. (VI) is similarly reduced and then acetylated to acetamidodiketo-octahydrophenanthroline, decomp. $>310^\circ$ (hydrochloride of the corresponding amine, m.p. $>360^\circ$). (VII) is transformed by $\text{POCl}_3\text{-PCl}_5$ into 2:3:6:7-tetrachloro-1:5-anthrazol-

ine, m.p. $\sim 300^\circ$ (decomp.) after softening at $\sim 260^\circ$, which is converted by HI-AcOH-red P at $150\text{--}173^\circ$ into 1:5-anthrazoline monohydrate, m.p. $240\text{--}242^\circ$ after softening at 228° (picrate, indef. m.p.). A method of preparing Raney Ni in the laboratory is described. H. W.

Constitution of tri-indole. O. SCHMITZ-DUMONT and J. TER HORST [and, in part, H. MÜLLER] (Annalen, 1939, 538, 261—282).—"Tri-indole" is probably 2-3'-indoliny-3-2''-indolinyindole (I). Carbethoxy-tri-indole (II) is stable at $> \text{m.p. } (163^\circ)$, but in hot



AcOH slowly gives carbethoxydi-indole [2-1'-carbethoxy-3'-indolinyindole] and indole, confirming the presence of the di-indole skeleton in (I). Inability of 3-methylindole to give more than a dimeride indicates union of ring C to position 3 of ring A. Presence of 3 active H in (I) is confirmed by prep. of 1:1'-dinitroso-1''-carbethoxy- (III), m.p. 142° (decomp.), and -1''-benzoyl-tri-indole, m.p. $159\text{--}160^\circ$ (decomp.), although (I) gives only a $(\text{NO})_2$ -derivative; the structure of the NO-derivatives is proved by conversion of dinitrosoacetyl-tri-indole into acetyltri-indole, and attachment of the acyl to N of ring B is proved by fission of (II). With MeI and anhyd. K_2CO_3 in COMe_2 , (I) gives 2-1':2'- or 2-1':3'-dimethyl-3'-indoliny-3-2''-indolinyindole (IV), m.p. $165\text{--}166^\circ$ [2 active H; picrate, m.p. 181° ; maleate, m.p. $168\text{--}170^\circ$; $(\text{NO})_2$ -derivative, m.p. $113\text{--}114^\circ$], which, when distilled, partly decomposes to give indole. With BrCN (IV) gives N-cyano-2'- or -3'-methyltri-indole, m.p. 230° ; in hot AcOH it gives indole; with Zn-HCl-AcOH it gives a (?) dimethyl-tetrahydrodi-indole, m.p. 178.5° . With iso- $\text{C}_5\text{H}_{11}\text{I}$ and K_2CO_3 in COMe_2 (I) gives a N-isoamyl derivative, m.p. 153.5° (2 active H), which yields a methylisoamyl derivative, m.p. $141\text{--}141.5^\circ$ [2 active H; $(\text{NO})_2$ -derivative, m.p. 245° (decomp.)]. With KOH-EtOH at room temp. (III) gives carbethoxydehydrotri-indole [3-2'-indolyl-2-1'-carbethoxy-2''-indolinyindole] (V), m.p. 201° (decomp.), and an orange-red substance (? VI), $\text{C}_{24}\text{H}_{17}\text{ON}_3$, m.p. $373\text{--}374^\circ$ (corr.; decomp. from 369°). (VI) is also obtained from (V) by KOH-EtOH or by thermal decomp., is reduced with difficulty (Na in boiling $\text{C}_5\text{H}_{11}\text{OH}$ only) to an auto-oxidisable leuco-compound, with PhNCO gives an orange-yellow compound, decomp. (?) 350° or 310° , or a red compound, decomp. $356\text{--}361^\circ$ (both are $\text{C}_{31}\text{H}_{22}\text{O}_2\text{N}_4$), with $\text{Ac}_2\text{O-NaOAc}$ gives a Ac_3 derivative, m.p. $298\text{--}300^\circ$ (decomp.), with $\text{NaNO}_2\text{-AcOH-C}_5\text{H}_5\text{N}$ gives a substance, $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3$, m.p. $320\text{--}322^\circ$ (decomp.) after sintering, and with $\text{NaNO}_2\text{-AcOH}$ gives a substance, $\text{C}_{24}\text{H}_{18}\text{O}_4\text{N}_4$, m.p. $302\text{--}305^\circ$ (decomp.) (Ac derivative). Tri-7-methylindole

behaves abnormally; it gives no benzoate or maleate, and its Me_2 derivative, m.p. $197\text{--}198^\circ$, does not react with BrCN; it gives a Ac_2 , m.p. 205° , and Ac_3 derivative (VII), m.p. 264° ; with ClCO_2Et and K_2CO_3 it gives a CO_2Et -derivative, m.p. $124\text{--}125^\circ$. Dinitrosoacetyltri-7-methylindole, m.p. 171° (decomp.; sinters at 168°), in hot EtOH gives (VII). R. S. C.

Dinuclear condensation products from alloxan and 3-amino-2-anilinopyridine. H. RUDY and O. MAJER (Ber., 1939, 72, [B], 940—945).—3-Amino-2-anilinopyridine (I) and alloxan in hot 30% AcOH give alloxan-2-anilino-3-pyridyl-5-imide (I), m.p. 255° (block; decomp.), which can be cryst. by cautious use of AcOH- H_2O , $\text{HCO}_2\text{H-H}_2\text{O}$, or $\text{C}_5\text{H}_5\text{N}$ but is isomerised by protracted use of these reagents (best by acids) to 2-keto-1-phenyl-1:2-dihydro-8-azaquin-oxaline-3-carboxureide (III), m.p. 252° (decomp.; bath pre-heated to 220°), which does not fluoresce in ultra-violet light and is not affected by CH_3N_2 in MeOH-Et $_2\text{O}$ or $\text{COMe}_2\text{-Et}_2\text{O}$. (III) is relatively stable towards mineral acids but is readily degraded by dil. alkali through the moderately stable 1-phenyl-1:2-dihydro-8-azaquin-oxal-2-one, m.p. 245° to (I). 9-Phenyl-8-azafavin could not be obtained from (II) or (III) by boiling with anhyd. AcOH- H_3BO_3 , $\text{HCO}_2\text{H-H}_3\text{BO}_3$, or ZnCl_2 or with AcOH- H_2SO_4 containing H_3BO_3 ; melting with $\text{H}_2\text{C}_2\text{O}_4$ is ineffective. Xanthhydrol does not ppt. (II) or (III). H. W.

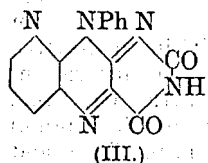
Constitution of yeast-ribonucleic acid. II. Guanine-uridylic acid. R. FALCONER, J. M. GULLAND, G. I. HORDAY, and (Miss) E. M. JACKSON (J.C.S., 1939, 907—915).—Samples of yeast-ribonucleic acid supplied by certain firms yield on aq. hydrolysis guanine-uridylic acid (I) (purified through its Pb salt), whereas those supplied by others do not (cf. Brederick *et al.*, A., 1936, 868; Tipson *et al.*, A., 1939, II, 128). This implies the existence of two types of nucleic acid, possibly interconvertible, and throws doubt on the conclusion of Brederick that (I) is a secondary product of the procedure used in its prep. (I) may contain a P-NH linking or an ester linking between the phosphoryl radical and the lactim form of the CO-NH linking of guanine; the balance of evidence seems to be in favour of the former, since in Van Slyke determinations of NH_2 , guanine, its derivatives, phenylphosphorylguanine (prepared from guanine and PPhCl_2), and (I) undergo deamination at 0° and 20° . On the other hand, comparison of the stabilities towards alkali of (I) and analogous compound shows that (I) is much less stable than would be expected from the presence of P-NH. Determinations of NH_2 in various nucleotides and nucleic acids are recorded. It is also demonstrated that the group in ribonucleic acids shown by Gulland *et al.* (A., 1938, III, 1051) to be resistant to enzymic fission is not that which unites the components of (I), and enzyme experiments with phenylphospho-amide and -anilide and monophenylphosphorylbenzamidine (Na salt) are recorded. F. R. S.

Azo-derivatives of chemotherapeutic compounds of the sulphonamide type with diuretic compounds of the purine group. F. P. MAZZA and C. MIGLIARDI (R. C. Atti Accad. Lincei, 1939, [vi], 29, 80—83).— $p\text{-NH}_2\text{-C}_6\text{H}_4\text{SO}_2\text{NH}_2$ (I) diazotised

and poured into theophylline in 10% NaHCO_3 gives 8-benzeneazothetheophylline-4'-sulphonamide (II), m.p. 121° (decomp.), reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to aminothetheophylline. 8-Benzeneazothetobromine-4'-sulphonamide, m.p. 93° (decomp.), and 8-benzeneazothetheophylline-4'-sulphonanilide-4''-sulphondimethylamide, m.p. 146° (corr.), are prepared similarly. All three compounds are protective to mice against β -haemolytic streptococci. Unlike (I), (II), injected intravenously, is absorbed into the lymph, where in 30 min. it reaches the same concn. as in the blood (0.02%), and remains after 1 hr., when it is no longer in the circulatory system.

E. W. W.

9-Phenyl- and 9-cyclohexyl-azaflavin. H. RUDY and O. MAJER (Ber., 1939, 72, [B], 933—939).—Alloxan (I) condenses with 3-amino-2-anilino-2-pyridine (II) in boiling glacial AcOH containing H_3BO_3 (ZnCl_2 is not necessary) to 9-phenyl-8-azaflavin (III), complete decomp. $335\text{--}340^\circ$ (bath preheated to 310°). It is unusually unstable since it is rapidly decomposed in hot AcOH in absence of light and does not survive dry heating at 100° . It is more sensitive than most flavins towards alkali hydroxide, readily giving (II). In boiling AcOH (I) and 3-amino-2-cyclohexylaminopyridine (III) afford 9-cyclohexyl-8-azaflavin (V), complete decomp. $320\text{--}325^\circ$ when placed in a bath preheated to 310° and then rapidly heated. It is relatively stable towards acids and oxidising agents but is degraded by alkalis. It is decomposed in visible light in the absence of air without yielding a substance with blue fluorescence; this is formed in presence of air and hence is a consequence of photolysis and oxidation. Exposure in a SiO_2 vessel to the unfiltered light of a Hg arc causes a blue-green fluorescence, one of the products acting as oxidising agent. Chromatographic treatment of the products obtained by use of a 200-w. lamp in presence of air shows the presence of ~ 5 components. The most weakly adsorbed substance, $(\text{C}_9\text{H}_7\text{O}_2\text{N}_3)_n$, m.p. $350\text{--}355^\circ$ (decomp.) in bath preheated to 310° , is characterised by a blue-green fluorescence visible in daylight in neutral or AcOH solution; before the quartz lamp this changes to bright yellow on addition of NaOH. (IV), b.p. $190^\circ/12$ mm., m.p. 119° [picrate, m.p. 210° (decomp.)], is obtained from 2-chloro-3-aminopyridine and cyclohexylamine at $200\text{--}210^\circ$. It gives a blue fluorescence when dissolved in AcOH or mineral acid; this disappears on addition of alkali. H. W.



(III.)

Phthalocyanines and allied compounds. R. P. LINSTAD (Ber., 1939, 72, [A], 93—103).—A lecture.

Heterocyclic compounds containing nitrogen. XLIII. Di- and tri-acetylbenzene and *p*-phenylenediglyoxal. P. RUGGLI and E. GASSENMEIER (Helv. Chim. Acta, 1939, 22, 496—511).—

$m\text{-C}_6\text{H}_4(\text{COCl})_2$ in C_6H_6 is converted by EtOH-free $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ into Et_2 isophthalaldiacetate, b.p. $150\text{--}158^\circ/15$ mm., m.p. 99° , converted by NH_3 -EtOH at 60° into Et_2 isophthalaldiacetate, hydrolysed and decarboxylated by boiling 15% H_2SO_4 to $m\text{-C}_6\text{H}_4\text{Ac}_2$, m.p. $31\text{--}32^\circ$ (dibenzylidene, m.p. 142° , dianisylidene, m.p. 135° , disalicylidene, blackens

$>150^\circ$, and divanillylidene, blackens $>200^\circ$, derivatives). $p\text{-C}_6\text{H}_4\text{Ac}_2$ (I) is converted by Cl_2 in AcOH at room temp. (without irradiation) into *p*-di(chloroacetyl)benzene, m.p. 153° . In boiling CHCl_3 under the influence of light (I) is converted by Cl_2 according to the duration of the experiment into *p*-chloroacetyl-dichloroacetyl-, m.p. 147° , *p*-di(dichloroacetyl)-, m.p. 143° , *p*-dichloroacetyltrichloroacetyl-, m.p. 136° , and di(trichloroacetyl)- (A), m.p. $120\text{--}121^\circ$, benzene. Br and (I) in AcOH afford *p*-di(bromoacetyl)benzene (II), m.p. 173° ; in various media further halogen atoms could not be introduced even with an excess of Br. KI and (II) in EtOH-AcOH yield *p*-di(iodoacetyl)benzene, m.p. 135° , which is transformed by NH_2Ph in warm EtOH into *p*-di(anilinoacetyl)benzene, blackens at $>200^\circ$. (I), NaOEt, and amyl nitrite in EtOH afford oximino-, m.p. 142° , and with a larger excess of reagents, di-oximino-, decomp. 165° , *p*-diacetylbenzene, which give resins when hydrolysed. SeO_2 in boiling Ac_2O transforms (I) into *p*-phenylenediglyoxal dihydrate (III), m.p. $110\text{--}111^\circ$ (decomp.), less advantageously obtained from KOAc and (A) in boiling EtOH; the diphenylhydrazone, decomp. 210° , disemicarbazone, m.p. 246° (decomp.), dianil, m.p. 155° , and diquinoxaline derivative, $\text{C}_{22}\text{H}_{14}\text{N}_4$, m.p. 262° , are described. Catalytic hydrogenation (Raney Ni in EtOH- H_2O at 50°) of (III) gives *p*-dihydroxyacetylbenzene, of which the (impure) benzoate, m.p. 85° , and semicarbazone, m.p. 226° , are described. Addition of HNO_3 (*d* 1.52) to (I) in Ac_2O at $>5^\circ$ yields 2-nitro-*p*-diacetylbenzene (IV), m.p. 46° , whereas conc. H_2SO_4 and HNO_3 (*d* 1.52) transform (I) into 2:6-dinitro-*p*-diacetylbenzene, m.p. $160\text{--}163^\circ$. Oxidation of (IV) with SeO_2 in boiling dioxan affords oily or resinous 2-nitrophenylene-1:4-diglyoxal, characterised by a pulverulent disemicarbazone, m.p. 251° (decomp.), and diphenylhydrazone, decomp. $\sim 100^\circ$. It is reduced (Raney Ni in dioxan and 95% EtOH at 50°) to non-cryst. 2-aminophenylene-1:4-diglyoxal, which gives a trisemicarbazone, decomp. $\sim 280^\circ$, and a triphenylhydrazone and is converted by Ac_2O at $50\text{--}60^\circ$ into non-cryst. (?) 6-glyoxalylindolone, characterised by a powdery monosemicarbazone and monophenylhydrazone. Isatin, (I), and 30% NaOH in EtOH at 100° afford *p*-phenylenedicinchonnic acid, m.p. 315° (decomp.) [Na_2 and $(\text{NH}_4)_2$, m.p. $\sim 337^\circ$ (decomp.)], darkens at 270° , salts]. 1:3:5- $\text{C}_6\text{H}_3\text{Ac}_3$ gives a triphenylhydrazone, m.p. $183\text{--}185^\circ$, and trisemicarbazone, decomp. 340° . It is converted by Br in AcOH into 1:3:5-tribromoacetylbenzene, m.p. 111° ; higher bromination could not be effected. SeO_2 in hot dioxan oxidises 1:3:5- $\text{C}_6\text{H}_3\text{Ac}_3$ to 1:3:5-triglyoxalylbenzene ($+9\text{H}_2\text{O}$), m.p. $117\text{--}118^\circ$ (trianil, decomp. $\sim 340^\circ$; triphenylhydrazone, blackens $\sim 90^\circ$; trisemicarbazone, decomp. $300\text{--}303^\circ$; tri-quinoxaline derivative, m.p. $302\text{--}303^\circ$). H. W.

Thiazolinephenols [hydroxyphenylthiazolines]. 5-Methyl- and 5:5-dimethyl-thiazolinephenols, by-products, and derivatives. W. F. HART and J. B. NIEDERL (J. Amer. Chem. Soc., 1939, 61, 1145—1148).—Repeated saturation of a mixture of a phenol and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{NCS}$ (I) or $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\text{NCS}$ (II) with HCl at room temp. during 1—4 weeks gives $\sim 50\%$ yields of 2-*p*-hydroxy-

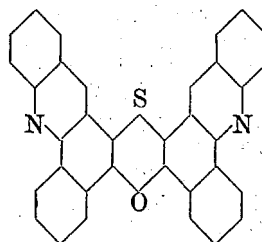
aryl-5-methyl- or -5:5-dimethyl-thiazolines, respectively. Poorer yields are obtained by AlCl_3 or H_2SO_4 . PhOH and (I) give also some β -p-hydroxyphenyl-n-propylisothiocarbimide, m.p. 150° . With H_2SO_4 (II) gives some 2-thiol-5:5-dimethylthiazoline (III), m.p. 162° , whether or not phenols are present. The following are new. 2-6'-Hydroxy-m-tolyl-, m.p. 134° (hydrochloride, m.p. 220° ; picrate, m.p. 159°), 2-3':4'-dihydroxyphenyl-, m.p. 136° (hydrochloride, m.p. 247° ; picrate, m.p. 188°), 2-2'-hydroxy-1'-naphthyl-, m.p. 65° (hydrochloride, m.p. 220° ; picrate, m.p. 169°), 2-5'-hydroxy-o-tolyl-, m.p. 131° [benzoate hydrochloride, m.p. 185 — 186° ; Me ether hydrochloride (prep. by NaOMe -MeOH, followed by Me_2SO_4 - C_6H_6 etc.), m.p. 159 — 160° ; p-nitro-, m.p. 87 — 88° (hydrochloride, m.p. 205°), and p-amino-benzoate, m.p. 142° (dihydrochloride, m.p. $>250^\circ$), 2-p-hydroxyphenyl-, m.p. 168° [$3'$ - NO_2 -, m.p. 135° (hydrochloride, m.p. 215°), reduced by SnCl_2 to the 3'- NH_2 -derivative (dihydrochloride, m.p. $>250^\circ$)], 5-methylthiazoline. 2-p-Hydroxyphenyl-, m.p. 181 — 182° (hydrochloride, m.p. 240° ; picrate, m.p. 190°), 2-5'-hydroxy-o-tolyl-, m.p. 134° (hydrochloride, m.p. 180 — 181° ; picrate, m.p. 186°), and 2-2':4'-dihydroxyphenyl-, m.p. 144 — 145° (hydrochloride, m.p. $>270^\circ$; picrate, m.p. 195°), -5:5-dimethylthiazoline. The products have PhOH coeff. <1 , but are potent anaesthetics, only slightly toxic, irritant as hydrochlorides, non-irritant as tartrates. The p-nitro-, m.p. 168° , and p-amino-benzoate (hydrochloride, m.p. 265°) of (III) and the derived disulphide, m.p. 162° , are prepared. R. S. C.

Preparation and reactions of some arylsulphonylbenzisothiazolones. R. G. BARTLETT, L. E. HART, and E. W. McCLELLAND (J.C.S., 1939, 760—762).—Condensation of the chlorination product of 2:2'-dithiobenzoyl chloride with arylsulphonamides gives 1-arylsulphonylbenzisothiazolones; the same substances and 2-arylsulphonyloxybenzisothiazoles are formed from arylsulphonyl chlorides and the unsubstituted benzisothiazolone. The 1-aryl compounds undergo fission with NaOH to the corresponding disulphides and acid hydrolysis eliminates the arylsulphonyl group. The following are described: 1-p-toluene-, m.p. 207° (oxidised with H_2O_2 to N-p-toluenesulphonyl-o-benzoic sulphinide, m.p. 214°), 1-benzene-, m.p. 218° , 4-chloro-1-benzene-, m.p. 205° , 4:6-dichloro-1-benzene-, m.p. 162° , and 4-chloro-1-p-toluene-sulphonylbenzisothiazolone, m.p. 203° ; 2-benzene-, m.p. 68° , and 2-p-toluene-sulphonyloxybenzisothiazole, m.p. 96° ; 2:2'-bis-p-toluene-, m.p. 218° , 2:2'-bisbenzene-, m.p. 225 — 227° , and 4:4'-dichloro-2:2'-bisbenzene-sulphonylcarbamyldiphenyl disulphide, m.p. 225° ; and (by heating with NH_2Ph) 2-anilinothiobenzobenzene-, m.p. 167° , 2-anilinothiobenzo-p-toluene-, m.p. 187° , and 5-chloro-2-anilinothiobenzenesulphonamide, m.p. 167° . F. R. S.

Isosteric and structurally similar compounds.
XI. Preparation and properties of 2:2'-dithiazolyl. H. ERLENMEYER and E. H. SCHMID (Helv. Chim. Acta, 1939, 22, 698—700; cf. A., 1939, II, 39).—2-Bromothiazole is converted by Cu powder in p-cymene at 170 — 180° into 2:2'-dithiazolyl, m.p. 102.5° . This is a much weaker base than 2:2'-dipyridyl (I), with which it does not form mixed crystals.

Unlike (I) it shows little tendency to form complex salts with Fe^{+++} . H. W.

Polycyclic condensed systems with heterocyclic rings. V. VI. 1:2:3:4:6:7-Tribenzacridine. W. BORSCHKE and F. SINN (Annalen, 1939, 538, 283—292, 292—298; cf. A., 1939, II, 227).—V. 2-Phenylquinoline-3-carboxylic acid and H_2SO_4 at 100 — 110° give 50% of 2:3-benz-4-aza-9-fluorenone.



(I.)

2-Phenylquinoline-3-acetic acid and SOCl_2 , followed by AlCl_3 , give 3:4:6:7-dibenzodiquinolono-2':3':2'':3''-2:1:8:9-phenoxthionine (I), m.p. 367 — 370° (decomp.) (cf. Borsche et al., A., 1937, II, 520), and attempts to prepare a benzacridine failed. β -2-Phenyl-3-quinolylpropionic acid (prep. from $\text{Bz} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ and o- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ in aq. NaOH), m.p. 169° , could not be cyclised; with glutaric anhydride and AlCl_3 it gives only a little $[\text{CH}_2]_3\text{Bz}_2$. 4-Phenylcarbostyryl-3-carboxylic acid (modified prep.) (Et ester, m.p. 199° ; benzanilide, m.p. 278°) and H_2SO_4 give 85% of 1-hydroxy-2-aza-3:4-benz-9-fluorenone, m.p. $\sim 340^\circ$ (decomp. from $\sim 310^\circ$). 4-Phenylquinoline-3-carboxylic acid (prep. from the Me ester of the 2-Cl-acid by HI-red P), m.p. 226 — 228° (picrate, m.p. 196° ; Me ester, m.p. 116 — 117°), and SOCl_2 , followed by AlCl_3 in PhNO_2 , yield 2-aza-3:4-benz-9-fluorenone, m.p. 216 — 217° [oxime, m.p. 261° (decomp.)]; 2:4-dinitrophenylhydrazon, m.p. 290° (decomp.), also obtained by H_2SO_4 at 105° and reduced by $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 200° to 2-aza-3:4-benzfluorene, m.p. 96° . o- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$ and $\text{CH}_2\text{Ac} \cdot \text{CO}_2\text{Et}$ at 150° give 3-acetyl-4-phenylcarbostyryl, m.p. 251 — 252° [oxime, m.p. 256 — 258° (decomp.)]; 2:4-dinitrophenylhydrazon, m.p. 291 — 293° (decomp.). o- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$ with $\text{CH}_2\text{Bz} \cdot \text{CO}_2\text{Et}$ at 160° , $(\text{CH}_2 \cdot \text{COMe})_2$ at 150° , or COPhMe and 5% KOH-EtOH at 100° gives 3-benzoyl-4-phenyl-, m.p. 259 — 260° , 4-phenyl-2-acetonyl-, m.p. 113 — 115° , and 2:4-diphenyl-carbostyryl, m.p. 114° (lit. 112° and 106 — 107°), respectively.

VI. 2-Phenyl-3-o-aminophenyl-5:6-benzoquinoline-4-carboxylic acid (prep. by H_2 -Pd-C in dil. NaOH from the NO_2 -acid), m.p. 206 — 210° (decomp.), could not be decarboxylated, probably owing to betaine formation; above the m.p., decomp. is total. β - $\text{C}_{10}\text{H}_7 \cdot \text{NH}_2$, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, and o- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ in hot EtOH give variable yields of 3-phenyl-2-o-nitrophenyl-5:6-benzquinoline-4-carboxylic acid (II) (up to 59% yield), m.p. 278° (decomp.), and the isomeric diketopyrrolidine, m.p. 237° (decomp.). Hydrogenation of (II) gives the NH_2 -acid, m.p. 284° (decomp.), decarboxylated, when heated, to yield 3-phenyl-2-o-aminophenyl-5:6-benzquinoline-, m.p. 201° , the diazonium sulphate from which in hot, dil. H_2SO_4 affords 1:2:3:4:6:7-tribenzacridine, m.p. 244 — 246° . With SOCl_2 , followed by AlCl_3 in PhNO_2 , (II) gives 4-o-nitrophenyl-3-azanaphtha-1':2'-1:2'-fluoren-9-one, m.p. 228° [2:4-dinitrophenylhydrazon, m.p. 298° (decomp.)], hydrogenated (Pd-C) in $\text{C}_5\text{H}_5\text{N}$ to the NH_2 -ketone (III), m.p. 260 — 265° ; and much

of the (?) azo- or azoxy-compound, m.p. 345—348°. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 190—200° reduces (III) to 4-o-aminophenyl-3-azanaphtha-1':2':1:2-fluorene, m.p. 236°, but further ring-closure by diazotisation etc. could not be effected. $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$, $\text{CH}_3\text{Ph} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, and $\text{o-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ give only 21% of 3-phenyl-2-o-nitrophenyl-7:8-benzquinoline-4-carboxylic acid, m.p. 294° (decomp.). R. S. C.

Erythrina alkaloids. III. Isolation and characterisation of a new alkaloid, erythramine. K. FOLKERS and F. KONIUSZY (J. Amer. Chem. Soc., 1939, 61, 1232—1235; cf. A., 1937, II, 434).—Many species of *Erythrina*, particularly *E. sandwicensis*, Deg., and *E. subumbrans* (Hassk.), Merrill, contain erythramine (I), $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$, m.p. 103—104°, b.p. 125°/0.00039 mm., $[\alpha]_{\text{D}}^{25} + 227.6^\circ$ in EtOH [hydriodide, m.p. 249° (decomp.), $[\alpha]_{\text{D}}^{25} + 220^\circ$ in H_2O ; hydrobromide, m.p. 228°, $[\alpha]_{\text{D}}^{25} + 203.2^\circ$ in H_2O ; hydrochloride, m.p. (+0.5 H_2O) 249°, (anhyd.) 250° (decomp.)], which has no curare-like action. Hypaphorine, $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2$, m.p. 236—237° (decomp.), $[\alpha]_{\text{D}}^{25} + 113.1^\circ$ in H_2O [nitrate, m.p. 223.5—224.5° (decomp.) (lit. 215—220°, 220°); hydrochloride, m.p. 231—232° (decomp.) (lit. 227°), $[\alpha]_{\text{D}}^{25} + 89.6^\circ$ in H_2O], also has no curare-like action, but is converted by MeI-NaOH in MeOH into $\text{Me } \alpha\text{-dimethylamino-}\beta\text{-3-indolylpropionate methiodide}$, m.p. 200.5—201.5° (decomp.) (lit. 197°), which has such action. R. S. C.

Anæsthetising action of convolvine and convolvamine. M. S. RABINOVITSCH and R. A. KONOVALOVA (J. Gen. Chem. Russ., 1939, 9, 41—58).—Convolvine in CHCl_3 and $(\text{CH}_2)_2\text{O}$ (4 hr. at 60°) yield *N-}\beta\text{-hydroxyethylconvolvine}*, m.p. 128—129° [hydrochloride, m.p. 235—237°; picrate, m.p. 212—214°; benzoate, m.p. 131—133° (hydrochloride, m.p. >250°; picrate, m.p. 214—216°)]. Nortropine (I) in PhMe and $\text{NEt}_2 \cdot (\text{CH}_2)_2 \cdot \text{Cl}$ (II) (at the b.p.) yield *N-}\beta\text{-diethylaminoethylnortropine}*, m.p. 59—61° [picrate, m.p. 160—162°; hydrochloride, m.p. 200—201°; hydrochloride of benzoate, m.p. 228—229° (decomp.)]. (I) and $\text{p-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ (III) in CHCl_3 (6 hr. at the b.p.) afford *O-p-nitrobenzoylnortropine*, m.p. 223—224°, reduced to *O-p-aminobenzoylnortropine*, m.p. 201—202° [hydrochloride, m.p. 222—224° (decomp.)]. Nortropidine (IV) and $(\text{CH}_2)_2\text{O}$ in CHCl_3 (5 hr. at 45—55°) give *N-}\beta\text{-hydroxyethylnortropidine}*, b.p. 140—141°/17 mm. [benzoate, m.p. 187—188°; p-nitrobenzoate, m.p. 60—62° (hydrochloride, m.p. 209—210°; picrate, m.p. 225—226°); p-aminobenzoate, m.p. 96—96.5° (hydrochloride, m.p. 206—207°; picrate, m.p. 150—151°); p-butylaminobenzoate, m.p. 66—68° (hydrochloride, m.p. 149—151°); phenylurethane (hydrochloride, m.p. 182—183°; phenylacetate, m.p. 113—114°)]. (IV) and (II) in PhMe (at the b.p.) yield *N-}\beta\text{-diethylaminoethylnortropidine}*, an oil (picrate, m.p. 173—175°). Tropine in PhMe and (III) (8 hr. at 120°) yield *p-nitrobenzoyltropine*, m.p. 135—136°, reduced (Fe in AcOH) to *p-aminobenzoyltropine*, m.p. 149—150° [hydrochloride, m.p. 250°; monopicrate, m.p. 230° (decomp.); dipicrate, m.p. 173—175°; acetate, m.p. 171—172°; phenylacetate, m.p. 143—145°], which with Ac_2O (5 hr. at 100°) gives *p-acetamidobenzoyltropine*, m.p. 151—152° (hydrochloride, m.p. >250°; phenylacetate, m.p. 141—142°). ψ -Tropine

and (II) in PhMe (4 hr. at 130—140°) give *p-nitrobenzoyl-}\psi\text{-tropine}*, m.p. 126—127°, reduced (Fe in AcOH , at 60°) to *p-aminobenzoyl-}\psi\text{-tropine}*, m.p. 163—165° (phenylacetate, m.p. 116—117°; hydrochloride, m.p. >235°). Tropine and $\text{CH}_2\text{Ph} \cdot \text{COCl}$ in CHCl_3 (4.5 hr. at 120—125°) yield *phenylacetyltropine*, an oil (hydrochloride, m.p. 198—200°). Tropine and PhNCO in Et_2O (3 hr. at the b.p.) give *tropine phenylurethane*, m.p. 170—171.5° (hydrochloride, m.p. >270°). Tropine and $\text{p-NHBu} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ (V) in PhMe (8 hr. at 110°) afford *p-butylaminobenzoyltropine*, m.p. 89—90° (hydrochloride, m.p. >270°); with ψ -tropine (4 hr. at 140—150°) the product is *p-butylaminobenzoyl-}\psi\text{-tropine}*, m.p. 109—111° (hydrochloride, m.p. >270°). Both the anæsthetising and the toxic action of convolvine are lowered by *N*-substitution, and are raised by introduction of NH_2 into the Bz radical; NHAc has a feeble, and NHBu a stronger, action than has NH_2 . Derivatives with a free OH group are only slightly toxic, but have no anæsthetising action, and the same applies to derivatives not possessing an ester group. The toxicity of ψ -tropine is < that of tropine derivatives with an equal anæsthetising action. The anæsthetising action of phenylacetates is > that of hydrochlorides. R. T.

Strychnos alkaloids. CVI. Methylations in the series of ψ - and 9-monohydroxy-brucine, and migrations of methyl between oxygen and nitrogen. H. LEUCHS and K. TESSMAR (Ber., 1939, 72, [B], 965—972).—Under stated conditions ψ -brucine Me ether and MeI afford *N-methylsec-}\psi\text{-brucine methiodide}* (I), decomp. 220—222° after softening [methoperchlorate (II), decomp. 280—285° after softening], hydrogenated (PtO_2 in H_2O) to a H_2 -derivative, m.p. 252—254° (decomp.) (perchlorate). ψ -Brucine is transformed by boiling MeI into the *hydriodide* of a *tert.* base. ψ -Brucine and 30 parts of boiling MeI give *N-methylsec-}\psi\text{-brucine hydriodide}*, m.p. 222—224° (decomp.) after softening; the free base, m.p. 228—230° (perchlorate, decomp. 210—215° after softening at 195°), is hydrogenated (PtO_2 in 0.2*N*- HCl) to a H_2 -derivative, m.p. 235—237° (vac.) (perchlorate, decomp. ~215° after softening), which is indifferent towards MeI or $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ but is converted by $\text{BaCO}_3\text{-Me}_2\text{SO}_4$ followed by 2*N*- HClO_4 into (II). (I) is transformed by NaOMe-MeOH into the *tert.* ether base (III), $\text{C}_{25}\text{H}_{30}\text{O}_5\text{N}_2$, m.p. 225° (vac.), converted by dil. HClO_4 into (II); it gives a *methiodide*, m.p. 245—247° (decomp.), and a *methoperchlorate*, m.p. ~288° (decomp.). The *methiodide* is hydrogenated (PtO_2 in H_2O) to the *tert.* base, $\text{C}_{26}\text{H}_{34}\text{O}_5\text{N}_2$, m.p. 175° (vac.) (perchlorate), which gives a *methiodide* (IV), m.p. 275—278° (decomp.) (perchlorate). The *hydriodide* of (III) is reduced (Na-Hg in H_2O) to the hydrogenated *tert.* base (V), $\text{C}_{25}\text{H}_{32}\text{O}_5\text{N}_2$, m.p. 184—185° (vac.) [perchlorate, m.p. 215° (decomp.) after softening at 200°; *methiodide* (VI), m.p. 203—204° (vac.), whence the *methoperchlorate*, m.p. ~285° (much decomp.)]. (III) is reduced by Na-Hg to (IV). Hydrogenation and Emde fission of (VI) gives a non-cryst. base (perchlorate, $\text{C}_{26}\text{H}_{38}\text{O}_5\text{N}_2 \cdot \text{HClO}_4$, m.p. ~145° after softening at 100°). Similar treatment of the *methiodide* of (III) gives a basic resin, transformed by MeI into (IV). H. W.

Delphinine. II. Oxo-[keto]-delphinine. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1939, 128, 431—437).—Delphinine (I) heated at 200—215° in H_2 yields *pyrodelphinine*, $C_{31}H_{41}O_7N$, m.p. 208—212°. Oxidation of (I) with $KMnO_4$ in $COMe_2$ yields α -keto-delphinine (II), $C_{33}H_{43}O_{10}N$, m.p. 218—221°, $[\alpha]_D^{20}$ —62° in $AcOH$, —55° in $EtOH$, apparently identical with X-214° of Keller (A., 1925, i, 830), and β -keto-delphinine (III), $C_{33}H_{43}O_{10}N$, m.p. 228—229°, $[\alpha]_D^{20}$ +31° in $AcOH$. Hydrogenation (H_2 - PtO_2 in $AcOH$) of (II) gives *hexahydro- α -ketodelphinine*, m.p. 195°; when heated in H_2 at 220°, (II) yields *pyro- α -ketodelphinine*, $C_{31}H_{39}O_8N$, which when heated with HCl - $MeOH$ yields an *isomeride*, m.p. 280—284°, and on hydrogenation (PtO_2 in $AcOH$) gives *hexahydro-pyro- α -ketodelphinine*, m.p. 183—185°. When heated at 100° with HCl - $MeOH$, (III) gives CO_2 and a *substance*, $C_{32}H_{43}O_9N$, m.p. 220—222°. J. D. R.

Aconite alkaloids. II. Formula of oxonitine. W. A. JACOBS, R. C. ELDERFIELD, and L. C. CRAIG (J. Biol. Chem., 1939, 128, 439—446).—Analyses of oxonitine (I) and its isomeride, formed by oxidation ($KMnO_4$ - $COMe_2$ - $AcOH$) of aconitine, indicate a formula of $C_{32}H_{43}O_{12}N$ as suggested by Späth *et al.* (A., 1931, 243) and not $C_{32}H_{41}O_{12}N$ as suggested by Majima and Tamura (A., 1937, II, 38). Aconitine is reduced (PtO_2 - H_2 in $EtOH$) to *hexahydroaconitine* (*perchlorate*, m.p. 209—210°), which is hydrolysed by H_2O at 160° to *hexahydrobenzoic acid* and *aconine*. Reduction of (I) in $AcOH$ with PtO_2 - H_2 gives *hexahydro-oxonitine* (II), m.p. 253°, and on heating in H_2 at 280—285° gives *pyro-oxonitine* (III), m.p. 180° (lit. 231°), which is hydrogenated in $EtOH$ to *hexahydropyro-oxonitine* (IV), m.p. 160—163°. When heated with 6% HCl - $MeOH$ at 100°/18 hr., (I) yields CO_2 and a *base*, m.p. 250°, $C_{31}H_{45}O_{10}N$ or $C_{32}H_{47}O_{10}N$, which contains 5 OMe and 1 NMe . Analyses of (II), (III), and (IV) support the formula proposed for (I). J. D. R.

Diphenylfluoroarsine. M. SARTORI and E. RECH (Annali Chim. Appl., 1939, 29, 128—130).— $AsPh_2Cl$ with AgF in C_6H_6 affords *diphenylfluoroarsine*, m.p. 17—19°, b.p. 157.5°/8 mm., which with aq. KOH or HNO_3 yields *bis(diphenylarseno)oxide* and *diphenylarsinic acid*, respectively. F. O. H.

Arsenated phenoxybutanols. W. F. HOLCOMB and C. S. HAMILTON (J. Amer. Chem. Soc., 1939, 61, 1236—1237).— p - OH - C_6H_4 - AsO_3H_2 and *isobutylene oxide* in $NaOH$ at 80° give p - β -hydroxyisobutoxyphenylarsinic acid, m.p. 189—192° (*Na salt*, m.p. >325°), converted by HNO_3 (d 1.5) in H_2SO_4 at 0° into 3-nitro-4- β -hydroxyisobutoxyphenylarsinic acid, m.p. 210—215°, and thence by $FeCl_2$ - $NaOH$ at 20° or H_2 -Raney Ni in aq. $NaOH$ at 4 atm. into the 3- NH_2 -acid, m.p. (anhyd.) 150—155°, (+ H_2O) 65—70°. The usual methods then yield 3-amino-4- β -hydroxyisobutoxyphenylarsine oxide, + H_2O , m.p. 123—124°, 4:4'-di- β -hydroxyisobutoxy, m.p. 135—140°, and 3:3'-diamino-4:4'-di- β -hydroxyisobutoxyarsenobenzene, m.p. 125—130°. R. S. C.

Relative reactivities of organometallic compounds. XXVI. Interconversion of bismuth and alkali metals. H. GILMAN, H. L. YABLUNKY, and A. C. SVIGOON (J. Amer. Chem. Soc., 1939, 61,

1170—1172; cf. A., 1939, II, 253).— $Bi(C_6H_4R)_3$ ($R = p$ - Me , p - Cl , p - OEt , o - OEt ; m.p. 121—122°) and 3 mols. of $LiBu^a$ give $BiBu^a_3$ and Li - C_6H_4R , carboxylation of the mixture yielding C_6H_4R - CO_2H ($R = p$ - Me 70, p - Cl 90, p - OEt 27.4, o - OEt 64%). $Bi(C_{10}H_7-2)_3$ reacts similarly, yielding 48.1% of α - $C_{10}H_7$ - CO_2H . $Bi(C_6H_4Me-p)_3$ and $NaBu^a$ (3 mols.) in light petroleum at 35° give $BiBu^a_3$ (46%) and p - C_6H_4Me - CO_2H (33%; by CO_2). Atm. oxidation of $BiBu^a_3$ is explosive; it gives small amounts of an aldehyde. R. S. C.

Formation of organochromium compounds from complex salts of chromium. F. HEIN (J. pr. Chem., 1939, [ii], 153, 160—176).—The compounds $[Cr(OH_2)_6](NO_3)_3 \cdot 3H_2O$ and $[Cr(OH_2)_6](OAc)_3$ are indifferent towards $MgPhBr$; the complex-bound H_2O is not attacked. $[Cr_3(OAc)_6(OH_2)_2](OAc)_3 \cdot H_2O$ is readily attacked; after reaction of the externally united H_2O an isomerisation to the non-electrolytic complex $[Cr_3(OAc)_9] \cdot 2H_2O$ is assumed. $K_3[Cr(C_2O_4)_3]$, $(NH_4)_3[Cr(C_2O_4)_3]$, and $Na[Cr(OEt)_4]$ are indifferent, showing that the homopolar linking of all acidic residues is not in itself sufficient to permit the formation of organometallic compounds but that the complex must also be without charge. The Cr complexes with CH_2Ac_2 , CH_2Ac - CO_2Et , *pæonol*, *hydroxyquinoline*, o - OH - C_6H_4 - $COMe$, and *xanthic acid* give $CrPh$ compounds whereby the only differences observable are in the readiness and vigour of the reaction under otherwise comparable conditions. In contrast, the classically internally complex salts $^+Cr \cdots NH_2 \cdot CH_2 \cdot CO_2^-$ and $^+Cr_3 \cdots NH_2 \cdot CHMe \cdot CO_2^-$ are passive towards Grignard's reagents; possibly these complexes have mainly the open structure, $^+Cr(NH_2 \cdot CH_2 \cdot CO_2)_3$ and $^+Cr(NH_2 \cdot CH_2 \cdot CO_2)_3$, the lattice forces being mainly of an electrostatic character and saturation occurring between the positive Cr end of a zwitterion and the negative NH_2 -acid end of another. The Cr lakes of alizarin, quinizarin, and 1-hydroxyanthraquinone are indifferent towards $MgPhBr$. The Et_3O solution of $[CrCl_3 \cdot 3H_2O]$ reacts smoothly with $MgPhBr$. H. W.

Cystine content of deaminised proteins. W. C. HESS and M. X. SULLIVAN (J. Biol. Chem., 1939, 128, 93—99).—The cystine content (determined by the Sullivan method) of wool deaminised by HNO_2 is about 25% < that of the original protein. When determined by the method of Okuda or of Vickery and White the cystine vals. are approx. those of the original protein. Part of the cystine combined in the protein is apparently deaminised by HNO_2 and converted into a compound, presumably $[S \cdot CH_2 \cdot CH(OH) \cdot CO_2H]_2$, giving the Okuda and Vickery and White but not the Sullivan reactions. Similar results with casein and lactalbumin are reported. W. O. K.

Mechanism of catalytic action of selenium in Kjeldahl nitrogen determination.—See A., 1939, I, 384.

Modified Beilstein test for halogens in volatile organic compounds. W. L. RUGH (Ind. Org. Chem. [Anal.], 1939, 11, 250).—The liquid to be tested is added dropwise to a heated 125-c.c. flask through

which passes the gas feed to a Bunsen burner the flame of which passes through a Cu gauze 4 cm. above the burner. The limit of sensitivity for $\text{CH}_2\cdot\text{CHCl}$ is 30 p.p.m. F. N. W.

Unstable isotopes. I. Determination of radioactive isotopes in organic material. E. CHARGRAFF (J. Biol. Chem., 1939, 128, 579—585).—Radioactivities of substances spread in thin layers on Al trays or dissolved in suitable solvents were determined by a Geiger-Müller counter using the β -ray radiation of the unstable isotope ^{40}K of KF as standard. Applications to the determination of radioactive P in Na_2HPO_4 , lecithin, etc. are described. T. F. D.

Analysis of hydrocarbon mixtures (boiling in the gasoline range), using thiolacetic acid to remove olefines. H. HOGG and E. EICHWALD (Rec. trav. chim., 1939, 58, 481—492).— $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) (300% of theoretical amount) and a synthetic mixture of 80% $n\text{-C}_7\text{H}_{16}$ and 20% Δ^8 -octene (II) react at room temp. (1 hr.) if EtCO_2H is used as solvent; decrease in olefine content is observed by determination of Br val. The hydrocarbon mixture must first be freed from peroxides by aq. FeSO_4 . Similar mixtures are examined, using the following in place of (II): Δ^8 -pentene; $\text{CMe}_2\cdot\text{CHMe}$; Δ^8 -hexene; β - or γ -methyl- Δ^8 -pentene; $\beta\gamma$ - or $\gamma\gamma$ -dimethyl- Δ^8 -butene; Δ^8 -heptene; β -methyl- Δ^8 -hexene; $\beta\gamma$ - (III), $\beta\delta$ - (IV), and $\delta\delta$ -dimethyl- Δ^8 -pentene (V); $\text{CMeBu}^+\cdot\text{CH}_2$; Δ^8 -octene; $\text{CHMe}\cdot\text{CMeBr}^+$; $\text{CMe}_2\cdot\text{CMePr}^+$ (VI); $\text{CH}_2\text{Bu}^+\cdot\text{CMe}\cdot\text{CH}_2$; cyclohexene (VII), and Δ^8 -hexadiene (VIII). Normal olefines, C_5 to C_8 , and those with one Me (C_5 to C_8) are readily removed, as is (VII). (III), (IV), (VI), and (VIII) are only partly removed, but almost completely with 475% of (I) for 48 hr. (V) is not removed at all, even with 500% of (I) for 70 hr. at 0° to 50° , with HCO_2H , AcOH , $\text{Pr}^+\text{CO}_2\text{H}$, or Pr^+CHO ; attempted catalysis with (II), P_2O_5 , AlCl_3 , etc., or salts of (I), also failed. There is no general rule for removal of olefines. After removal, the quantities of aromatic, paraffin, and naphthene hydrocarbons in the residual hydrocarbons are determined in the usual manner. A. T. P.

Identification of aldehydes and ketones. G. B. L. SMITH and T. G. WHEAT (Ind. Eng. Chem. [Anal.], 1939, 11, 200—201).—The Jamieson method (A., 1912, ii, 487) is applicable to the determination of N in semicarbazide, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$, and the semicarbazones of COPhMe , COMe_2 , COEt_2 , COPh_2 , PhCHO , $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, and cyclohexanone but fails with furfuraldehydesemicarbazone and thiosemicarbazide. F. N. W.

Semicarbazides. VIII. p -Xenylsemicarbazide as a reagent for identification of aldehydes and ketones. P. P. T. SAH and I. S. KAO (Rec. trav. chim., 1939, 58, 459—464; cf. A., 1937, II, 129).— $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$ (I) and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}_2$ in EtOH at 50° and then at 25° , or (I) and KCNO in aq. AcOH , give $p\text{-xenylcarbamide}$, m.p. 196° , converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH into $p\text{-xenylsemicarbazide}$, m.p. $275\text{--}277^\circ$, which reacts with CO-compounds in 95% EtOH + a trace of AcOH . $p\text{-Xenylsemicarbazones}$ of the following are prepared: MeCHO , m.p. $208\text{--}209^\circ$; EtCHO , m.p. $186\text{--}188^\circ$; Pr^+CHO , m.p.

$180\text{--}181^\circ$; Pr^+CHO , m.p. $176\text{--}177^\circ$; Bu^+CHO , m.p. $148\text{--}149^\circ$; $n\text{-C}_5\text{H}_{11}\cdot\text{CHO}$, m.p. $135\text{--}136^\circ$; $n\text{-C}_6\text{H}_{13}\cdot\text{CHO}$, m.p. $177\text{--}178^\circ$; $n\text{-C}_7\text{H}_{15}\cdot\text{CHO}$, m.p. $175\text{--}176^\circ$; $n\text{-C}_8\text{H}_{17}\cdot\text{CHO}$, m.p. $179\text{--}180^\circ$; $n\text{-C}_9\text{H}_{19}\cdot\text{CHO}$, m.p. $171\text{--}172^\circ$; PhCHO , m.p. $232\text{--}234^\circ$; $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. $235\text{--}236^\circ$ (decomp.); o -, m.p. $268\text{--}270^\circ$, and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, m.p. $204\text{--}205^\circ$; furfuraldehyde, m.p. $228\text{--}229^\circ$; COMe_2 , m.p. $220\text{--}221^\circ$; COMeEt , m.p. $200\text{--}201^\circ$; $\text{COMe}\cdot\text{C}_6\text{H}_{13}\cdot\text{n}$, m.p. $147\text{--}148^\circ$; $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$, m.p. $231\text{--}232^\circ$; COPhMe , m.p. $224\text{--}225^\circ$; $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, m.p. $227\text{--}228^\circ$; COPh_2 , m.p. $187\text{--}188^\circ$; cyclopentanone, m.p. $235\text{--}237^\circ$; camphor, m.p. $273\text{--}274^\circ$; $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, m.p. $179\text{--}180^\circ$; levulinic acid, m.p. $203\text{--}204^\circ$; Et , m.p. $164\text{--}165^\circ$, and CH_2Ph laevulate, m.p. $151\text{--}152^\circ$. A. T. P.

Azides. XI. β -Naphthazide and β -naphthyl carbimide as reagents for identification of phenols. P. P. T. SAH (Rec. trav. chim., 1939, 58, 453—458; cf. A., 1937, II, 360).—Anhyd. β -naphthazide (I), refluxed in dry ligroin until evolution of N_2 ceases, affords $\beta\text{-C}_{10}\text{H}_7\cdot\text{NCO}$ (II), m.p. $\sim 57^\circ$. (I) or (II) and ArOH in boiling ligroin give β -naphthylurethanes of the following: PhOH , m.p. 149° ; o -, m.p. $127\text{--}129^\circ$, m -, m.p. 123° , and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}$, m.p. 159° ; 3:4:1-, m.p. $148\text{--}149^\circ$, 2:5:1-, m.p. $143\text{--}145^\circ$, and 2:4:1- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{OH}$, m.p. 140° ; o -, m.p. $136\text{--}137^\circ$, m -, m.p. $116\text{--}117^\circ$, and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, m.p. $169\text{--}170^\circ$; o -, m.p. 128° , m -, m.p. $118\text{--}119^\circ$, and $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$, m.p. $175\text{--}176^\circ$; o -, m.p. $150\text{--}152^\circ$, m -, m.p. 148° , and $p\text{-C}_6\text{H}_4\text{I}\cdot\text{OH}$, m.p. 189° ; 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{OH}$, m.p. 166° ; 2:4:1- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{OH}$, m.p. $150\text{--}151^\circ$; $s\text{-C}_6\text{H}_2\text{Cl}_3\cdot\text{OH}$, m.p. $161\text{--}162^\circ$; $s\text{-C}_6\text{H}_2\text{Br}_3\cdot\text{OH}$, m.p. $181\text{--}183^\circ$; o -, m.p. $120\text{--}121^\circ$, m -, m.p. 124° , and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. $172\text{--}173^\circ$; o -, m.p. $108\text{--}109^\circ$, m -, m.p. $93\text{--}95^\circ$, and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m.p. 167° ; α -, m.p. $174\text{--}175^\circ$, and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, m.p. $202\text{--}203^\circ$; thymol, m.p. $140\text{--}141^\circ$, and isothymol, $89\text{--}91^\circ$; Me, Et, and benzyl salicylate, char and decomp. at 290° , $295\text{--}296^\circ$, and $299\text{--}300^\circ$, respectively. All m.p. are corr. A. T. P.

Standardisation of 2:6-dichlorophenol-indophenol for ascorbic acid titration. O. H. KEYS (Ind. Eng. Chem. [Anal.], 1939, 11, 293; cf. A., 1938, III, 217).—Priority for Dick is claimed. F. N. W.

Micro-determination of sugar with α -naphthol. K. YAMAFUJI and T. YOSHIDA (Biochem. Z., 1939, 301, 61—64; cf. Ujsághy, A., 1938, III, 1066).—The sugar solution, after purification with basic Pb acetate, is mixed with 20% $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}\text{--EtOH}$ and conc. H_2SO_4 . After 3 min. the mixture is rapidly cooled and its colour compared with those of standard solutions [mixtures of $\text{Co}(\text{NO}_3)_2$ and CoSO_4 or of rhodamine, erythrosin, toluidine-blue, and tartrazine]. When the sugar concn. is < 1 mg.-%, 0.05% aq. FeCl_3 having the same colour as the sugar- $\text{C}_{10}\text{H}_7\cdot\text{OH}$ mixture is used in conjunction with the standard solution. W. McC.

Micro-determination of glutaric acid.—See A., 1939, III, 639.

Determination of cholesterol and its esters. I. Precipitation of cholesterol-digitonin complex in water-acetone-trichloroethylene med-

ium. II. New method of extraction of "total cholesterol." Liebermann's reaction as basis for determination. Rapid determination of ratio of esters to total cholesterol. M. PAGET and G. PIERRART (Bull. Soc. Chim. biol., 1939, 21, 528—536, 537—548; cf. A., 1937, III, 291; A., 1938, III, 262).—I. A method for the determination of 0.1—2 mg. of cholesterol (I), but not of amounts > 1 g. per l., is described. 1.5 c.c. of a 0.5% solution of digitonin (II) in a mixture of MeOH, EtOH, and $C_2H_5Cl_3$ is added rapidly to 5 c.c. of a solution of (I) in $C_2H_5Cl_3$ at 100°. Heating is continued until ~3 c.c. of solvent is left (no MeOH), and then 6 c.c. of $COMe_2$ + 0.2 c.c. of H_2O is added slowly. The pptd. complex is washed twice with Et_2O . The filtrate and Et_2O washings are evaporated to dryness and the residual (I) is determined colorimetrically (Liebermann). A solution of (I) in $C_2H_5Cl_3$ gives the reaction with H_2SO_4 and Ac_2O but the intensity of the colour is only ~half that obtained when $CHCl_3$ is used as solvent. For complete pptn. of (I) the time of reaction should be as short as possible and only a slight excess of (II) used. In the determination of total (I) and cholesterol esters by the method of Grigaut (A., 1933, 410; 1935, 1261), 6.5—29% of (I) does not dissolve and is therefore determined as esters. Also adsorption of esters on the complex occurs.

II. For determination of total (I), 2 c.c. of serum are added dropwise to a boiling mixture of 15 c.c. of $COMe_2$ and 5 c.c. of EtOH, with shaking. After addition of 8 c.c. of $C_2H_5Cl_3$ and shaking for 1 min. the mixture is filtered, an aliquot of the filtrate evaporated, and the residue dissolved in $CHCl_3$ or $C_2H_5Cl_3$ and determined colorimetrically. Liebermann's reaction should be performed at temp. ± 13 — 15° and readings taken after 30 min. For the determination of the ratio (r) of ester : total (I) the latter is extracted by Grigaut's method and, after removing Et_2O , the residue is analysed as above. The esters are determined colorimetrically in the filtrate and washings. The method is compared with those of Velluz (A., 1933, 1065) and Kanner (*ibid.*, 410, 1181) and the results for r agree with those obtained by the former.

J. N. A.

Bromine index of cinnamic [acid] derivatives.

A. LESPAGNOL, R. HERLEMONT, and G. STERN (J. Pharm. Chim., 1939, [viii], 29, 447—459; cf. A., 1937, II, 290).—A modification of the procedure of Volmar and Samdahl (B., 1928, 236) is described, excess of Br being allowed to act for 24 hr. in diffused light at room temp. The excess of Br is removed with H_2SO_3 . Good results are obtained with $CHPh:CH:CO_2H$, CH_2Ph and cinnamyl cinnamate. Immediate quant. removal of HBr from $CHBrPh:CHBr:CO_2H$ occurs when $AgNO_3$ is added, $CHPh:CHBr$ and unsaturated Br-acids being produced.

W. McC.

Determination of iodine in sodium tetraiodophenolphthalein. A. Q. BUTLER and R. A. BURDET (Ind. Eng. Chem. [Anal.], 1939, 11, 237—239).—The weighed sample (~0.2 g.) is dissolved in 15 c.c. of 5% aq. NaOH and digested (100°; $\frac{3}{4}$ hr.) with 25 c.c. of saturated aq. $KMnO_4$. After cooling and then adding 75 c.c. of H_2O and 10 c.c. of dil. H_2SO_4 , conc. aq. $NaHSO_3$ is added until the solution is

colourless, when 2 c.c. of glacial AcOH, ~1 g. of $(NH_4)_2CO_3$, and 1 c.c. of 0.5% EtOH-di-iodofluorescein are added prior to final titration with 0.1N- $AgNO_3$. The complete analysis requires 1 $\frac{1}{2}$ hr. and affords results comparable with those obtained by the Pregl micro-combustion method. F. N. W.

Hordenine reineckate. P. GONNARD (Bull. Soc. Chim. biol., 1939, 21, 617—619).—The salt, $C_{10}H_{15}ON(C_4H_6N_6SCr) \cdot 5H_2O$, m.p. 176—178° (decomp.), is prepared by adding a saturated solution of Reinecke salt (I) to one of hordenine in dil. acid (pH 4—4.5). The salt shows absorption in the infra-red, and has a large band in the yellow region with max. at 522 $m\mu$; absorption continues into the extreme ultra-violet after a min. at 232 $m\mu$. For the determination of hordenine, the salt prepared as described above is collected, washed with aq. (I) and then with Et_2O , and dissolved in a few c.c. of $COMe_2$. After removal of the latter, the residue is ignited to Cr_2O_3 , which is weighed. The error is ~1% and the solution must contain < 0.1 g. per 100 c.c. J. N. A.

Microchemical distinctive reactions for cocaine, novocaine, and stovaine. A. MARTINI and J. C. B. GRAF (Mikrochem., 1939, 26, 233—240).—Microchemical methods of detecting the three bases are reviewed. The picric acid method is unsatisfactory, as the crystals produced are very similar and in the case of novocaine may be very similar to those of picric acid. The Br- H_2O test for novocaine (A., 1933, 173) is sp., and its sensitivity is ~1 in 3000. K_2PbI_4 yields characteristic ppts. with all three bases. Treatment of the sample with 10% aq. KI and then an equal amount of 20% aq. $RhCl_3$ yields yellow and salmon crystals with cocaine and stovaine, respectively. With novocaine only an amorphous ppt. is obtained. The sensitivity of this test is ~1 in 10,000.

J. W. S.

Microchemistry of yohimbine. A. MARTINI (Mikrochem., 1939, 26, 227—232).—Previous methods of detecting yohimbine are neither sp. nor very sensitive. If aq. yohimbine hydrochloride is treated with a particle of KCN and heated the liquid becomes turbid after a few min. and after cooling long prisms are formed, bunched in feather shapes. The limiting concn. detectable by this method is 1 in 5000 and the min. quantity detectable 2 μg . Characteristic microcryst. ppts. are also obtained with $Na_2B_4O_7 \cdot 10H_2O$, Na_2SeO_3 , and Na_2TeO_3 (sensitivity 1 in 5000) and with $K_2C_2O_4 \cdot H_2O$ (sensitivity 1 in 3000). Yohimbine can be used for detection of $B_4O_7^{--}$, SeO_3^{--} , TeO_3^{--} , and $C_2O_4^{--}$.

J. W. S.

Semimicro-colorimetric determination of alkaloid poisons. M. DUQUENOIS (Ann. Falsif., 1939, 32, 95—97).—The alkaloids (extracted from viscera etc.) are dissolved in H_2O slightly acidified with HCl and are treated with a known excess of a solution of Reinecke salt (I), the prep. of which is described. After 1 hr. the pptd. reineckates are removed by filtration through sintered glass and the concn. of (I) in the filtrate is determined colorimetrically. The error of determination is $\pm 8\%$ with those alkaloids which are quantitatively pptd. by (I).

E. C. S.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1939.

"Condensation" of an organic molecule. M. FRÈREJACQUE (Bull. Soc. chim., 1939, [v], 6, 1008—1011).—A theoretical suggestion for determining "condensation," *i.e.*, total no. of rings + double linkings in the mol. of an org. compound. "Rings" corresponds with the no. of ruptures necessary to give a chain compound. Examples given in support are vitamin-*E*, -*B*₂, and -*B*₁, of "condensation" 5, 10, and 7, respectively. A. T. P.

Modes of vibration of normal aliphatic chains. J. BARRIOL (J. Phys. Radium, 1939, [vii], 10, 215—216).—Theoretical. Although it has been impossible to account satisfactorily for all the vibrations attributable to normal aliphatic chains, these seem to consist of (a) those in which the mol. behaves as the seat of a system of stationary waves, and (b) those in which the chain terminal groupings play the important rôle. W. R. A.

Hydrogen linkings in organic compounds. K. KUNZ (Angew. Chem., 1939, 52, 436—440).—A description is given of the application of the conception of the H linking to simple org. chemicals (fatty acids, MeOH, H₂C₂O₄) and to cases of linking within the mol. (CH₂Ac·CO₂Et; CH₂Ac₂). In the latter case a ring is produced which is possible only when the general geometrical requirements for the existence of a plane ring are present and the distance of H from the other atom is small. Except in the case of derritol strong H bridges are present only in six-membered rings. Detailed consideration is given to the *o*-, *m*-, and *p*-isomerides of the C₆H₆ series and to compounds of the type *o*-OH·C₆H₄·CHO. H bridges between OH and N are found in *o*-OH·C₆H₄·CH₂NPh and *o*-OH·C₆H₄·CH₂N·NHPh. The presence of a H linking may afford important evidence of steric structure. A chemical consequence of the presence of a H linking is the diminished activity of the OH group sometimes betrayed by the failure to give additive products with CPh₃Cl. H. W.

Physical constants of certain hydrocarbons and their structural isomerides. M. WOJCIECHOWSKI (Przemysł Chem., 1939, 23, 129—135).—The b.p. of the following hydrocarbons are: *n*-hexane 68·73°, *β*- 60·26°, and *γ*-methylpentane 63·25°, *ββ*-49·80°, and *βγ*-dimethylbutane 58·02°, *n*-heptane 98·41°, *ββ*- 79·2°, and *βγ*-dimethylpentane 89·9°, *γ*-ethylpentane 93·3°, *γ*-methylhexane 91·8°, *ββγ*-trimethylbutane 80·9°, *n*-octane 125·65°, *ββδ*-trimethylpentane 99·23°, *n*-nonane 150·81°, *β*- 143·2°, *γ*- 144·1°, and *δ*-methyloctane 142·4°, *βε*-, 135·21°, and *βζ*-dimethylheptane 135·2°, *o*- 144·50°, *m*- 139·10°, and *p*-xylene 138·44°. The vals. of the coeffs.

*d*0/*d**p* for the various isomerides of a given hydrocarbon do not differ significantly, showing that the val. of this coeff. depends on the no., but not on the arrangement, of atoms in a given mol. R. T.

Reactivity of lower hydrocarbons. VIII—XI. —See A., 1939, I, 422, 425.

Organic fluorine compounds. SCHERER (Angew. Chem., 1939, 52, 457—459).—A lecture.

Thermal decomposition of chloromercuric *β*-ethoxyethanesulphonate. J. D. LOUDON and N. SHULMAN (J.C.S., 1939, 1066—1067).—OEt·[CH₂]₂·SH in NaOH with 1:2:4-C₆H₃Cl(NO₂)₂ in dioxan yields 2:4-dinitrophenyl *β*-ethoxyethyl sulphide, m.p. 65—66°, oxidised by H₂O₂-AcOH to the sulphone, m.p. 97°, which when heated with piperidine in C₆H₆ followed by treatment with NaOH and HgCl₂ yields chloromercuric *β*-ethoxyethanesulphonate. On heating this alone, SO₂ is evolved; when heated in H₂O, C₂H₄ is formed, identified as *bis*-(2:5-dichlorophenylthio)ethane, m.p. 125°, also formed from (CH₂Br)₂ and 2:5:1-C₆H₄Cl₂·SH in aq. EtOH. J. D. R.

Common basis of intramolecular rearrangements. VI. Reactions of neopentyl iodide. F. C. WHITMORE, E. L. WITTLE, and A. H. POPKIN (J. Amer. Chem. Soc., 1939, 61, 1586—1590).—CH₂Bu⁺I reacts very slightly, if at all, with KCN, CH₃Na(CO₂Et)₂, NaOEt, KOPh, or dil. aq. or EtOH·KOH. With very conc. KOH (10 mols.)-EtOH at 180—190° it gives 70—80% of CMe₄, H₂, KI, and KOAc, with 12—13% of CH₂Bu⁺OEt, b.p. 90·5°/740 mm., and 3—5% of CH₂Bu⁺OH (*tert*.-C₅H₁₁·OH is unchanged by this treatment). With aq. AgNO₃ or Hg(NO₃)₂ it gives products, hydrolysed to *tert*.-C₅H₁₁·OH (97 and 80% yield, respectively). With KOAc in EtOH at 200° it gives 40—70% of CH₂Bu⁺OAc and 10—20% of olefines (mainly CHMe:CMe₂), and in AcOH 40 and 45%, respectively. CH₂Bu⁺I and *tert*.-C₅H₁₁Cl with ICl give complex mixtures, but CH₂Bu⁺Cl does not react. Reaction mechanisms are discussed. R. S. C.

Catalytic transformations of certain homologues of cyclopentane. B. A. KAZANSKI and S. R. SERGIENKO (J. Gen. Chem. Russ., 1939, 9, 447—452).—*n*-Butylcyclopentane passed with H₂ over Ni-Al₂O₃ at 250—305° yields *δ*-methyloctane and other hydrocarbons of lower mol. wt. *iso*Amylcyclopentane in N₂ passed over C-Pt at 310° yields hydrocarbons of lower b.p., including 38% of unidentified aromatic hydrocarbons. Similar results are obtained with H₂, in which case the products included *βε*-dimethyloctane. With Ni-Al₂O₃ similar results are

also obtained, but $C_{10}H_8$ was found in the catalysate. *sec*.-Butylcyclopentane in N_2 passed over Cr_2O_3 at 425° yields unsaturated 16–18% and aromatic hydrocarbons 11–13%. R. T.

Action of sulphuric acid on olefines. V. GUTRIIA (J. Gen. Chem. Russ., 1939, 9, 221–227).—The only product initially formed in 1 : 6 mixtures of alcohols (Pr^iOH , Bu^iOH , $iso-C_5H_{11}OH$) with 96% H_2SO_4 at $>5^\circ$ is alkyl sulphate. After 9 hr. small amounts of polymerised olefines are found. In uncooled solutions products of polymerisation, hydrogenation, and further dehydrogenation of the olefines are found. At 100° the yields of all these products rise, the highly unsaturated polymerides forming an asphaltous mass, which with further heating yields a porous coke; these processes are associated with copious evolution of SO_2 . It is concluded that hydrogenation cannot take place without simultaneous dehydrogenation, but that the latter reaction need not necessarily involve the former. Polymerisation is an entirely independent reaction. R. T.

1:2- and 1:4-Addition. III. Nitrogen trioxide and trimethylethylene. A. MICHAEL and G. H. CARLSON (J. Org. Chem., 1939, 4, 169–197; cf. A., 1937, II, 270).—Nitrous fumes, i.e., the moist gas from $As_2O_3-HNO_3$ ($d^{20} 1.43$), and CMe_2CHMe (I) in Et_2O give the dimeric nitrates of γ -nitroso- β -methylbutan- β -ol, $[CMe_2(O\cdot NO_2)\cdot CHMe(NO)]_2$ (II) (1%). (I) in absence of solvent, in N_2 , affords 40.5% of (II). (I) and HNO_3 ($d^{20} \sim 1.30$) affords some (II), $[NO_2\cdot CMe_2\cdot CHMe(NO)]_2$ (III), $NO_2\cdot CMe_2\cdot CHMe\cdot NO_2$ (IV), and γ -nitro- β -methyl- Δ^{β} -butene (V). (III) and “nitrous fumes” in C_6H_6 , or O_3 in $CHCl_3$, give (IV). (I) and N_2O_4 saturated with NO at -80° give (II) and (V). (III) or (IV) is reduced catalytically (PtO_2-AcOH or Ac_2O) to isoamylenediamine, whilst (II) similarly affords γ -amino- β -methylbutan- β -ol (p -toluenesulphonate, m.p. 127–129°; benzoate, m.p. 95–96°). The product described (*loc. cit.*) as $CMe_2(O\cdot NO)\cdot CHMe\cdot NO_2$, from N_2O_4 and (I), is (IV). Experiments under varied conditions show no consistency in the products of reaction. The “bis-trimethylethylene nitrosite” of Schmidt (A., 1903, i, 581) is probably (III). A. T. P.

Hydrogenation of hexene under high pressure. A. F. NIKOLAEVA and P. V. PUTSCHKOV (J. Gen. Chem. Russ., 1939, 9, 277–279).—Hexene and H_2 ($400^\circ/90$ atm.; MoS_2 catalyst) yield chiefly *n*-hexane, with some isohexane, which is also produced from *n*-hexane under the given conditions. R. T.

$\beta\gamma$ -Ditert.-butyl- Δ^{γ} -butadiene. H. J. BACKER (Rec. trav. chim., 1939, 58, 643–661).—The pinacol of pinacolin, m.p. 74.5° (A., 1938, II, 389), and PCl_3-CHCl_3 give $\beta\gamma$ -ditert.-butyl- Δ^{γ} -butadiene (I) [$\beta\beta\epsilon\epsilon$ -tetramethyl- $\gamma\delta$ -dimethylenehexane], b.p. 180° . The diol, m.p. 88° , also reacts similarly, but the unstable form, m.p. 69° (*loc. cit.*), gives only a small yield of (I). Ozonisation in aq. $CHCl_3$ affords HCO_2H and ditert.-butylglyoxal (oxime, m.p. 123°). (I) and $Br-CHCl_3$ at 0° give $\beta\beta\epsilon\epsilon$ -tetramethyl- $\gamma\delta$ -di(bromomethyl)- Δ^{γ} -hexene, $(CH_2Br\cdot CBr)_2$ (II), m.p. $96-97.5^\circ$ (crystallographic data), and a liquid dibromide, mainly $\gamma\delta$ -

dibromo- $\beta\gamma$ -ditert.-butyl- Δ^{α} -butene (δ -bromo- $\beta\beta\epsilon\epsilon$ -tetramethyl- δ -bromomethyl- γ -methylenehexane) (ozonisation gives HCO_2H). Ozonisation of (II) gives 2 mols. of bromopinacolin (identified as 2-acetamido-4-tert.-butylthiazole, m.p. $177-178^\circ$). (I) is hydrogenated (PtO_2 ; Et_2O) to $\beta\gamma$ -ditert.-butyl- Δ^{α} -butene [$\beta\beta\delta\epsilon\epsilon$ -pentamethyl- γ -methylenehexane] (III), b.p. $183-184.5^\circ$. Equimols. of (III) and BzO_2H in $CHCl_3$ at 0° , then at room temp., afford $\alpha\beta$ -oxido- $\beta\gamma$ -ditert.-butylbutane (IV), b.p. $81.5-83^\circ/9$ mm., which is isomerised by $H_2SO_4-Ac_2O$ or $HCl-EtOH$ to a mixture (V) of aldehyde + ketone, b.p. $91-94^\circ/11$ mm. or $75-92^\circ/9$ mm., respectively, which [as does (IV)] exposed in air or with H_2O_2-AcOH gives $\alpha\beta$ -ditert.-butylbutyric acid (VI), m.p. $94-95^\circ$ (*Tl* salt, m.p. $\sim 216-218^\circ$), formed from the aldehyde. (V) and $BzO_2H-CHCl_3$ give $BzOH$, (VI), and (?) γ -keto- $\beta\beta\epsilon\epsilon\zeta$ -pentamethylheptane, b.p. $88-92^\circ/10$ mm. (2:4-dinitrophenylhydrazones, m.p. $175-176^\circ$). Ozonisation of (III) in $EtOAc$ at -20° gives mainly (IV), b.p. $195-205^\circ$ (derived 2:4-dinitrophenylhydrazones, m.p. $172-174^\circ$); excess of O_3 gives HCO_2H and a little (VI); an ozonide, $C_{12}H_{24}O_3$, is also obtained. (I) and $BzO_2H-CHCl_3$ at 0° , then at room temp., give $\gamma\delta$ -oxido- $\beta\gamma$ -tert.-butyl- Δ^{α} -butene, b.p. $70-73^\circ/10$ mm. (derived 2:4-dinitrophenylhydrazones, m.p. $210-211^\circ$, probably from ketone), not hydrogenated at 80° . (I) is hydrogenated (PtO_2-AcOH) to $\beta\gamma$ -ditert.-butylbutane, b.p. $191-192^\circ$, which does not react with SO_3 or maleic anhydride. Theoretical aspects are discussed. (I) and NO_2 afford (?) $\alpha\delta$ -dinitro- $\beta\gamma$ -ditert.-butyl- Δ^{β} -butene, m.p. $132-133^\circ$. A. T. P.

Isomeric transformations of halogen derivatives of unsaturated aliphatic hydrocarbons. I. Action of hydrochloric acid on dimethylacetylenylcarbinol in presence of ammonium chloride and cupric or cuprous chloride. T. A. FAVORSKAJA (J. Gen. Chem. Russ., 1939, 9, 386–395).— $OH\cdot CMe_2\cdot C\equiv CH$ with HCl in aq. $EtOH$, in presence of NH_4Cl and $CuCl_2$, gives γ -chloro- γ -methyl- Δ^{α} -butinine, b.p. $74-76^\circ$, which is transformed in presence of $CuCl$ into α -chloro- γ -methylallene, b.p. $101-104^\circ$, and this further isomerises to α -chloro- γ -methyl- $\Delta^{\alpha\gamma}$ -butadiene, b.p. $97.5-98^\circ$. This condenses with maleic anhydride to 5-methyl-1:2-dihydrophthalic acid, m.p. $210-211^\circ$, its 2:5-endoethylene-dicarboxylic acid derivative, m.p. 353° , and two other unidentified acids, $C_7H_8(CO_2H)_2$, m.p. $239-241^\circ$, and $C_9H_{10}(CO_2H)_4$, m.p. 95° , solidifying at 110° and remelting at $298-299^\circ$. R. T.

Acetylene chlorohydrins and their corresponding dioxides and erythritols. N. A. GERSCHTEIN (J. Gen. Chem. Russ., 1939, 9, 361–368).— $COMe\cdot CH_2Cl$ and $(:C\equiv MgBr)_2$ in Et_2O yield $\alpha\zeta$ -dichloro- $\beta\epsilon$ -dimethyl- Δ^{γ} -hexene- $\beta\epsilon$ -diol, which could not be purified by distillation, owing to decomp. The diol treated with KOH yields two stereoisomeric dioxides, $(\begin{smallmatrix} CH_2 \\ | \\ O \end{smallmatrix} \text{---} CMe\cdot C\cdot)_2$, m.p. $44.5-45^\circ$, and b.p. $95-96^\circ/12$ mm., $104.5-105^\circ/18$ mm., respectively; these dioxides yield α -methylglyceric acid when oxidised ($KMnO_4$ or O_3), and give two isomeric $\beta\epsilon$ -dimethyl- Δ^{γ} -hexene- $\alpha\beta\epsilon\zeta$ -tetraols, m.p. $113.5-114^\circ$ (tetra-acetate, b.p. $171^\circ/6$ mm.) and $130-131^\circ$ (tetra-acetate, b.p.

193—194°/9 mm.), respectively, when kept with dil. HCl. R. T.

Preparation of primary alcohols by means of organo-magnesium derivatives. S. VEIBEL, F. LUNDQUIST, F. ANDERSON, and E. FREDERIKSEN (Bull. Soc. chim., 1939, [v], 6, 990—998).—MgRX and $(\text{CH}_2)_2\text{O}$ in Et_2O (best method A) give $\text{R}\cdot[\text{CH}_2]_2\cdot\text{OH}$, also prepared from MgRX and $(\text{CH}_2\text{O})_n$ in Et_2O at room temp. (method B) or in *isoamyl* ether at $\sim 150^\circ$ (method C for alcohols of b.p. $> 130^\circ$). Mechanisms of reactions are discussed. MgEtBr or MgPr²Cl (method A) gives BuOH (82%) or $\text{CH}_2\text{Bu}^2\cdot\text{OH}$ (60% yield), respectively. MgBu²Cl or CHMeEt·Mg·CH₂Br (method B) affords ββ-dimethyl- (40%) or β-methyl-propan-α-ol (36% yield), respectively. *n*-C₆H₁₃·OH and BuOH are prepared by method C, but A is preferable. A. T. P.

Preparation of methylallylcarbinol. L. STÖHR (Ber., 1939, 72, [B], 1138—1139).—Detailed modifications of the method of Pariselle (A., 1912, i, 331) permit the yield of the carbinol from MeCHO, allyl bromide, and Mg to be increased from 15% to 55%. H. W.

l-Citronellol. J. DÈUVRE (Compt. rend., 1939, 208, 1658—1660).—A mixture (I) of citronellol and geraniol is only partly reduced with Na—liquid NH₃. (I) with Cu at 215°/30 mm. gives citronellal + geraniol (no isomerisation), which when fractionally distilled affords 1-βζ-dimethyl-Δ⁸-octenaldehyde (l-citronellal), b.p. 86—87°/10 mm., $[\alpha]_{17}^{25} -6.21^\circ$, reduced (MgCl·OEt) to l-citronellol (II), b.p. 108—109°/10 mm., $[\alpha]_{18}^{25} -2.15^\circ$ [allophanate (III), m.p. 106—107°]. (II) with O₃ gives mainly COMe₂ and about 1% of CH₂O. (III) gives no CH₂O. J. L. D.

Diacetylenylcarbinol, OH·CH(C:CH)₂. R. LESPIEAU (Bull. Soc. chim., 1939, [v], 6, 947—949).—Excess of (C:MgBr)₂ and HCO₂Et in Et₂O at -10° give small yields of diacetylenylcarbinol, m.p. 51.5—52°. CH₂·CBr·CH(OH)·C:CH and KOEt give tars only. A. T. P.

Preparation of unsaturated higher alcohols. II. S. KOMORI (J. Soc. Chem. Ind. Japan, 1939, 42, 46—47B; cf. B., 1938, 1445).—Hydrogenation (Zn-Cr oxide at 330°/100 atm.) of the Et esters of erucic, oleic, physetoleic, linderic, and linoleic acids and of certain unsaturated oils yields 64—87% of the corresponding unsaturated alcohols, the yield increasing with increasing mol. wt. A. LI.

Fission of acetylene γ-glycols by potassium carbonate. A. T. BABAJAN (J. Gen. Chem. Russ., 1939, 9, 396—400).—The glycols are heated with K₂CO₃ at 150—170°, when the reactions (i) $\text{OH}\cdot\text{CRR}'\cdot\text{C:CH} + \text{CORR}' \leftarrow (\text{OH}\cdot\text{CRR}'\cdot\text{C})_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{CORR}'$ (ii) take place [R = Me, R' = Et, (i) 95, (ii) 5%; R' = (CH₂)₅, (i) 85, (ii) 15%; R = R' = Me, (i) 80, (ii) 20%; R = Me, R' = Ph, (i) 30, (ii) 70%; R = R' = Ph, (i) 0, (ii) 100%]. Glycols in which R or R' is Ph do not yield phenylurethanes. The phenylurethane of βε-dimethyl-Δ⁸-hexine-βε-diol, m.p. 203°, and of γζ-dimethyl-Δ⁸-octine-γζ-diol, m.p. 186—187° and 201—202° (stereoisomerides), are prepared. R. T.

Synthesis of isopropyl ether. V. Dehydration of isopropyl alcohol with sulphuric acid under pressure. VI. Comparison of the catalytic powers of dilute sulphuric acid, benzenesulphonic acid, naphthalene-2-sulphonic acid, phosphoric acid, and oxalic acid. M. KATUNO (J. Soc. Chem. Ind. Japan, 1939, 42, 59—62B; 62—65B; cf. A., 1938, II, 256).—V. Pr²OH with dil. H₂SO₄ at 140° under pressure yields less (40—47%) Pr²O than the continuous process at 1 atm. The production of C₃H₈ is reversible and increases with rise of temp.

VI. As catalysts for the dehydration of Pr²OH at 140° under pressure, conc. $>$ dil. H₂SO₄ $>$ aromatic sulphonic acids $>$ H₃PO₄. H₂C₂O₄ has no catalytic effect, but decomposes. The catalytic power of H₂SO₄ is unaffected by C₅H₅N, NH₂Ph, H₃BO₃, I, COMe₂, PhCHO, or CH₂O. A. LI.

Preparation of the pure sodium salts of higher alkyl sulphuric esters. W. KIMURA and H. TANIGUCHI (J. Soc. Chem. Ind. Japan, 1939, 42, 89B).—Treatment of the higher alcohols with H₂SO₄ or ClSO₃H in indifferent solvents gives only incomplete conversion into the alkyl H sulphate. The pure Na salt can be obtained by careful extraction of org. impurities, followed by recrystallisation. The times necessary for complete hydrolysis of Na lauryl, myristyl, cetyl, and stearyl sulphates on boiling with N-HCl have been investigated. J. W. S.

Synthesis of potassium and sodium γ-hydroxy-octane-α-sulphonate. R. L. SHRINER, H. A. RENDLEMAN, and A. BERGER (J. Org. Chem., 1939, 4, 103—105).—Cl·[CH₂]₄·CHO and Me[CH₂]₄·MgBr give, through Me·[CH₂]₄·CH(O·MgBr)·[CH₂]₂·Cl, α-chlorooctan-γ-ol, b.p. 110—115°/14 mm.; NaI·COMe₂ then gives α-iodooctan-γ-ol, converted by refluxing with Na₂SO₃ or K₂SO₃ in aq. EtOH into Na (11%) or K (15% yield) γ-hydroxyoctane-α-sulphonate, respectively. Neither salt is converted into the free acid or corresponding sultone (cf. Baldeschweilder *et al.*, A., 1929, 1423), through the Ca or Ba salt, or by HCl·ROH, 50% H₂SO₄, or H₂PtCl₆. A. T. P.

Synthesis of diallylacetate acid [heptadiene-carboxylic acid]. M. DOMINIKIEWICZ and M. KIRAWSKA (Arch. Chem. Farm., 1939, 4, 41—45).—Diallylacetate acid (I) is obtained in 74% yield by the reactions: $\text{CHNaAc}\cdot\text{CO}_2\text{Et} + \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$ (II) $\rightarrow \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ (+Na) [+ (II)] $\rightarrow (\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2\text{CAc}\cdot\text{CO}_2\text{Et}$, which is heated with conc. KOH in EtOH, to yield chiefly (I), with a small amount of diallylacetone. R. T.

Fatty acids obtained by oxidation of a synthetic paraffin. F. RENNKAMP (Z. physiol. Chem., 1939, 259, 235—244).—Oxidation of the paraffin yields a mixture of acids, which are converted into triglycerides. The resulting solid mixture, which contains only very small amounts of unsaturated acids, is hydrolysed and the acids are converted into Me esters, which after fractional distillation in vac. are hydrolysed to the acids. A series of normal fatty acids, probably octoic to behenic acid, is thus obtained. Acids with odd and even no. of C are present in approx. equal amounts. The following have been

isolated: decoic, undecoic, lauric, tridecoic, myristic, pentadecoic, palmitic, heptadecoic, stearic, and benenic acids. C_{12} , C_{13} , C_{14} , and C_{15} acids constitute 50—60% of the total acid mixture. J. N. A.

Male sex hormones. VIII. Activators of male hormones. I. A. OGATA, S. HIRANO, and T. KON (J. Pharm. Soc. Japan, 1938, 58, 57—58).—Trimethylene glycol dipalmitate (I), m.p. 56.5°, is obtained from the glycol and palmitic acid (II) (even with a small amount). Propylene glycol dipalmitate (III), m.p. 69.5—70°, is prepared using 2 mols. of (II) or 1 mol. of the chloride. $(CH_2-OH)_2$ (1 mol.) with (II) (1 mol.) gives the mono- (IV), m.p. 51—52.5°, and di-palmitate (V), m.p. 69—70°. The activity of testosterone (50 μ g.) is considerably enhanced by daily injection of (III) (20 mg.) or (V) (30 mg.); (IV) (30 mg.) has no appreciable effect whilst (I) (2.5 mg.) and (V) (5 mg.) appear to retard the activity. H. B.

Higher aliphatic compounds. VIII. Purification of oleic and elaidic acids. Binary systems from oleic, elaidic, palmitic, and stearic acids. Technique of low-temperature crystallisation. J. C. SMITH (J.C.S., 1939, 974—980).—Fractional distillation of Me oleate followed by hydrolysis and fractional crystallisation from $COMe_2$ at -40° to -50° gives oleic acid (α), f.p. 13.34°, m.p. 13.36° $\pm 0.04^\circ$, and (β), m.p. 16.25°, which is isomerised by HNO_3 - $NaNO_2$ to elaidic acid, m.p. 43.68° $\pm 0.05^\circ$ after crystallisation from EtOH at -5° . Binary systems of elaidic-stearic, oleic-stearic, oleic-palmitic, and elaidic-palmitic acid are described. The systems are all of the eutectic type, and in the oleic-stearic system the eutectic is reached at 2—3% of stearic acid. None of the systems gives in the liquidus curve any indication of compound formation. The technique of, and apparatus for, crystallisation at low temp. are described. J. D. R.

Enolisation of pyruvic acid. F. ARNDT, M. OZANSOY and H. ÜSTÜNYAR (Rev. Fac. Sci. Istanbul, 1939, 4, 83—87).— $AcCO_2Me$ with CH_2N_2 at room temp. gives (almost quantitatively) Me α -oxido- α -methylpropionate, b.p. 61°/19 mm. (with 5% of high-boiling product, but no O.Me ether), which with MeOH-HCl yields the *chlorohydrin*, b.p. 81°/14 mm. Me diphenylenepyruvate with CH_2N_2 yields an O.Me ether, m.p. 60° (? + a little of the ethylene oxide). The evidence for and against enolisation of $AcCO_2H$ is discussed. A. LI.

Action of nitrous acid on α -substituted γ -butyrolactones. V. V. FEOFILAKTOV and A. S. ONISCHTSCHENKO (J. Gen. Chem. Russ., 1939, 9, 304—313).— α -Aceto- γ -butyrolactone and aq. HNO_2 yield anti- α -oximino- γ -butyrolactone (I), by way of an unstable α -NO-derivative. (I) is similarly obtained from γ -butyrolactone- α -carboxylic acid (II), the Et ester of which gives α -nitroso- α -carbethoxy- γ -butyrolactone (III), m.p. 97—98° (decomp.), with aq. HNO_2 or with N_2O_3 . (III) and EtOH yield CO, NO, and a compound, $C_{20}H_{37}O_{12}N$, m.p. 162—163°, when heated, whilst with aq. NaOH the product is α -oximino- α -hydroxybutyric acid. $(CH_2)_2O$, $CN\cdot CH_2\cdot CO_2Et$, and NaOEt in EtOH at 50° yield α -cyano- γ -butyrolactone, b.p. 176—178°/8 mm., which

with HNO_2 gives a substance, $C_{10}H_9O_5N_3$, m.p. 177—178°.
R. T.

Degradations and thermal condensations of β -hydroxyethylenic compounds with particular reference of ricinoleic acid. A. BARBOT (Ann. Chim., 1939, [xi], 11, 519—605).—The residue obtained in the prep. of heptaldehyde (I) from castor oil is a glyceride (II) and does not contain hydroxy-undecoic acids. Alcoholysis of (II) permits the separation of heptoic, nonoic, undecenoic (III), palmitic, myristic, stearic, oleic, Δ^{9k} - (IV) and Δ^{9a} - (V) -linoleic, and ricinoleic (VI) acid, aldehydic, ketonic, and condensed acids. Variation in the composition of the residue and of the distillate during the course of pyrolysis shows that polymerisation is preceded by dehydration which results in the production of (IV) and (V). The observation that thermal degradation increases more rapidly than dehydration with temp. allows the determination of the most favourable conditions for the reaction, $Me\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH\cdot CH\cdot[CH_2]_7\cdot CO_2H = (I) + CH_2\cdot CH\cdot[CH_2]_8\cdot CO_2H$, and thus for the max. yield of (I). Polymerisation is the result of a diene condensation according to Diels' mechanism of (IV) with itself or with other ethylenic acids formed in the change, such as (III) or (V). At a high temp. the diene condensation is preponderating. The conditions most favourable for the production of aldehydes cause, by polymerisation, a partial loss of (III). Under certain conditions, however, the yield of (III) can be increased from 17% to 30% without appreciably diminishing that of (I). The Diels condensation is followed by the migration of H within the tetrahydrobenzenic mol. which has been formed; this results in the partial transformation into a benzenic compound with saturated side-chains. This observation, combined with a study of the degradation products, suggests that the condensed acids, dilinoleic and undecenoic-linoleic, are

$CH\cdot CH(C_6H_{13})\cdot CH\cdot CH_2\cdot CH\cdot CH\cdot C_5H_{11}$ and
 $CH\text{---}CHX\cdot CHX$
 $CH\cdot CH(C_6H_{13})\cdot CH\cdot CH_2X$
 $CH\text{---}CHX\cdot CH_2$ (X = $[CH_2]_7\cdot CO_2H$), respectively. Thermal degradation of (VI) or ricinoleic acid unexpectedly affords Δ^9 -octene and nonoic acid:

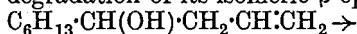
$Me\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH\cdot CH\cdot[CH_2]_7\cdot CO_2H = C_6H_{13}\cdot CH\cdot CH_2 + CO + Me\cdot[CH_2]_7\cdot CO_2H$. The two last compounds are formed by thermal scission of sebacaldehydic acid or its esters, which are thus intermediates in the degradation, which can be formulated:

$Me\cdot[CH_2]_5\cdot CH(OH)\cdot CH\cdot CH\cdot[CH_2]_7\cdot CO_2H = Me\cdot[CH_2]_5\cdot CH\cdot CH_2 + CHO\cdot[CH_2]_8\cdot CO_2H$. There is thus a mode of union between C_{19} and C_{10} of (VI) and the hydroxylic O which leads to the hypothesis of the structure, $C_6H_{13}\cdot CH\langle\begin{smallmatrix} CH_2 \\ OH \end{smallmatrix}\rangle CH\cdot CH\cdot[CH_2]_7\cdot CO_2H$.

Trimethylene oxides are little known but the hypothesis is supported by an examination of the general thermal stability of rings containing four atoms. Rupture of the β -epoxy-ring could then lead to the two observed modes of degradation. In verification it is shown that the thermal fission of diethyltrimethylene

oxide occurs: $\text{CH}_2\langle\text{CH}_2\text{CH}_2\rangle\text{O}$ (VII) = $\text{COEt}_2 + \text{C}_2\text{H}_4$ and (VII) = $\text{CET}_2\text{CH}_2 + \text{CH}_2\text{O}$. From the view-point of thermal stability the structures $\cdot\text{CH}:\text{CH}:\text{CH}_2\cdot\text{C}(\text{OH})\cdot$ and $\cdot\text{C}\langle\text{CH}_2\text{CH}_2\rangle\text{CH}:\text{CH}_2\cdot$ are equiv.

Thus, allylhexylcarbinol gives all the pyrolytic products which can be expected from the thermal degradation of its isomeric β -epoxide:



$\text{C}_6\text{H}_{13}\cdot\text{CH}\langle\text{CH}_2\text{CH}_2\rangle\text{CHMe}$ (VIII) $\rightarrow \text{C}_6\text{H}_{13}\cdot\text{CH}:\text{CH}_2 + \text{MeCHO}$ and (VIII) $\rightarrow \text{C}_6\text{H}_{13}\cdot\text{CHO} + \text{CH}_2\cdot\text{CHMe}$. All β -enolic compounds can undergo these two types of degradation by heat and by hydrolysing agents; this property is independent of the nature of the atoms A, B, and C constituting the group $\cdot\text{A}(\text{OH})\cdot\text{B}\cdot\text{C}$. This is confirmed by numerous examples. Nevertheless, the conditions under which these degradations are effected and the relative proportions of the two reactions do not show that the true β -epoxides are the intermediates of this degradation. Analogies of stability and structure prove that the mols. of β -enols are closely related sterically to the β -epoxides. The rules in accordance with which β -hydroxyethylenic compounds are degraded by heat or by alkalis are discussed.

H. W.

Interpretation of optical rotatory power of homologues of tartaric acid. Optical activity and chemical structure of tartaric acid. IX. Y. TSUZUKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 36, 31—46; cf. A., 1939, I, 357).—By analysis of the rotatory dispersions of various cyclic derivatives, $\text{CRR}'\langle\text{O}\cdot\text{CH}\cdot\text{CO}_2\text{R}''\text{O}\cdot\text{CH}\cdot\text{CO}_2\text{R}''\rangle$, it is shown that the negative partial rotation is due to the left hand portion of the mol. and the positive to the right hand portion. The effect of the $\text{CO}_2\text{R}''$ groups is < that of OH, possibly because the oxygens of the former are not directly attached to the asymmetric C. The rotatory dispersions of compounds substituted as follows have been measured in the visible region, most of them in the liquid state and some in solution in C_6H_6 or EtOAc or both: $\text{R} = \text{R}' = \text{R}'' = \text{Et}$; $\text{R} = \text{H}$, $\text{R}' = \text{CHPh}\cdot\text{CH}\cdot$, $\text{R}'' = \text{Et}$; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$, $\text{R}'' = \text{Et}$, Pr , Bu , CH_2Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Et}$, $\text{R}'' = \text{Me}$, Et , Pr^a , Pr^b , Bu ; and Et *o*-methylcyclohexylidene-*d*-tartrate. λ_0 in the equation $M = k/(\lambda^2 - \lambda_0^2)$ is less for C_6H_6 than for EtOAc solutions.

T. H. G.

*iso*Butyl *i*-tartrate.—See A., 1939, I, 411.

Acids of *Euphorbia biglandulosa*, Boiss., latex.

II. Structure of biglandulic acid. N. P. KIRJALOV (J. Gen. Chem. Russ., 1939, 9, 401—405).—Dihydrobiglandulic acid (A., 1939, II, 122) readily eliminates CO_2 when heated, yielding *dinic acid*, m.p. 129—131° (previously described as dihydrobiglandulobutane- $\alpha\beta\gamma$ -tricarboxylic acid, whence it is concluded that dinic acid is the γ -lactone of α -hydroxy- δ -methylpentane- $\gamma\delta$ -dicarboxylic acid. Biglandulic acid is the γ -lactone of α -hydroxy- δ -methyl- Δ^8 -pentene- $\beta\gamma\delta$ -tricarboxylic acid.

R. T.

Action of hot concentrated alkaline solutions on biglandulic acid. N. P. KIRJALOV (J. Gen. Chem. Russ., 1939, 9, 432—435).—Biglandulic acid heated with 50% KOH at 150—170° for 15 min. yields *isopropylidenesuccinic acid*, m.p. 161—162°, CO_2 , and HCO_2H .

R. T.

Saccharolactone. D. A. KORNIEENKO (Trans. Inst. Chem. Charkov Univ., 1938, 4, No. 13, 85—89).—Saccharolactone is prepared by Kiliani's method (A., 1923, i, 1059) with slight modifications. R. T.

Partial hydrolysis of the dichloride of sulpho-acetic acid. R. VIELLEFOSSE (Compt. rend., 1939, 208, 1406—1408).— $\text{SO}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$ (I) (1 mol.) with H_2O (1 mol.) in Et_2O at -10° gives *chlorosulphonyl-acetic acid* (II), m.p. 72—75°, which with nascent H gives H_2S , obtained probably by the reduction of $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The Et ester of (II), prepared either from (I) or (II), gives H_2S with nascent H. This reaction is given by SO_2Cl but not by SO_3H , which supports the structure (II) (cf. Bodendorf and Senger, A., 1939, II, 204). (I) or an ester when heated with the appropriate amine in presence of Li_2CO_3 gives *Me*, m.p. 112—113°, *Et*, m.p. 109—110°, and *Pr* *sulphon-2:2-dinaphthylamidoacetate*, m.p. 86—87°; *sulphon-2:2-dinaphthylamidoacet-2:2-dinaphthylamide*, m.p. 239—240°; *Et* *sulpho-2-naphthylanilidoacetate*, m.p. 105—106°; and *sulpho-2-naphthylanilidoacet-2-naphthylanilide*, m.p. 166—167° and 184—185°.

J. L. D.

Kinetics of decomposition of acetaldehyde-ammonia.—See A., 1939, I, 423.

Reduction of α -ethylenic aldehydes. J. WIE-MANN (Bull. Soc. chim., 1939, [v], 6, 1125—1126; cf. A., 1936, 589).—Reduction of $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$ (method: A., 1935, 608, 963; Mg used in this case) affords α - or γ -hydroxy- Δ^4 -hexene $\alpha\delta$ -oxide.

A. T. P.

Application of the Grignard reaction to Δ^4 -ketones. V. I. ESAFOV (J. Gen. Chem. Russ., 1939, 9, 467—470).—The product of condensation of $\text{CMe}_2\cdot\text{CH}\cdot\text{COMe}$ (I) and MgEtBr when distilled from $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ yields δ -methyl- β -ethyl- Δ^{4v} -pentadiene, b.p. 111—112°, with higher condensation products. Unidentified compounds of high mol. wt. are formed with MgPhBr and (I) or furfurylideneacetone.

R. T.

Formation of higher aliphatic ketones in the thermal decomposition of fat. L. W. J. HOLLEMAN and D. R. KOOLHAS (Rec. trav. chim., 1939, 58, 666—674).—The ketone, new m.p. 59.0°, obtained by Banzon (B., 1938, 811) is *n-pentacosan- μ -one* (I), $\text{C}_{11}\text{H}_{23}\cdot\text{CO}\cdot\text{C}_{13}\text{H}_{27}$, formed apparently by condensation of 1 mol. of lauric (II) and 1 mol. of myristic acid (III). A semicarbazone or arylhydrazide could not be prepared from (I), but the *oxime* (IV), m.p. 31° (prepared in KOH-EtOH), is rearranged (Beckmann) by Ac_2O (4 parts) and H_2SO_4 (1 part) at $< 70^\circ$ to the *N*-alkyl acid amide (V), m.p. 75°, hydrolysed by 96% H_3PO_3 (not by HCl or HBr) to (II), (III), undecyl- and tridecyl-amine (identified by their platinichlorides). (IV) and (V) are probably mixtures of the two geometrical isomerides. (I), m.p. 59.5—60°, synthesised from (II), (III), and Fe (method: Easterfield *et al.*,

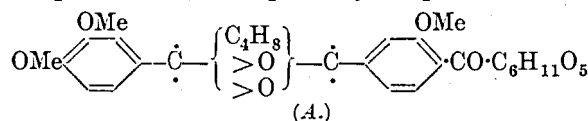
J.C.S., 1911, 99, 2298), is reduced by $\text{Na-C}_6\text{H}_{11}\text{-OH}$ to *n*-pentacosan- μ -ol, m.p. 70—71° (m.p. 67·5° from (I) from coconut oil). Coconut oil also affords some (?) di-*n*-amyl ketone. Pork fat (VI) heated with Fe also gives (I) and a product, m.p. 74—75°. (VI) alone at 200° for 25 hr. gives a little (I). A. R. P.

**2-Methyl-*l*-rhamnose and 2-methyl-*d*-fucose and their bearing on the configuration of digit-
alose.** H. B. MACPHERILL and R. C. ELDERFIELD (J. Org. Chem., 1939, 4, 150—161).— α -Methyl-*d*-galactoside and *p*- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl-C}_5\text{H}_5\text{N}$ give the 6-*p*-toluenesulphonate, converted into 3:4-isopropylidene- α -methyl-*d*-galactopyranoside 6-*p*-toluenesulphonate (modified method of Ohle *et al.*, A., 1933, 492), which gives (Purdie's reagents) the 2-*Me* derivative, m.p. 86—87°, converted by NaI-COMe_2 at 140° into 6-iodo-3:4-isopropylidene-2-methyl- α -methyl-*d*-galactopyranoside. This is reduced (Raney Ni in alkaline MeOH) to 3:4-isopropylidene-2-methyl- α -methyl-*d*-fucopyranoside, b.p. 77—78°/2 mm., converted into 2-methyl-*d*-fucose (I), m.p. 155—161° (varies with rate of heating), $[\alpha]_D^{25} + 87^\circ$ (const.) in H_2O . α -Methyl-*d*-fucopyranoside has m.p. 155—156°, $[\alpha]_D^{25} + 190\cdot0^\circ$ in H_2O (cf. Votček *et al.*, A., 1930, 326). The mixed α - and corresponding β -derivative and $\text{COMe}_2\text{-HCl-(MeCHO)}_3$ give the 3:4-isopropylidene derivative, m.p. 98—100°, successively methylated and hydrolysed (4% H_2SO_4) to (I). 3:4-Diacetyl-rhamnopyranoside 1:2-orthoacetate and HCl-MeOH at room temp. for 10 hr., then aq. Ag_2CO_3 , give β -methyl-*l*-rhamnopyranoside 2:3:4-triacetate, m.p. 150—151°, $[\alpha]_D^{25} + 46^\circ$ in $(\text{CHCl}_3)_2$, and a syrup, mainly 3:4-diacetyl-*l*-rhamnose 1:2-orthoacetate. Methylation (Purdie's reagents) then gives 2-methyl-methyl-*l*-rhamnopyranoside 3:4-diacetate, b.p. 116—118°/0·2 mm., converted by $\text{Ba(OMe)}_2\text{-MeOH}$ at 0° for 48 hr., then with H_2O (after saturation with CO_2) for 1 hr. at 100° (bath), into 2-methyl-methyl-*l*-rhamnopyranoside (probably a mixture of α - and β -glucosides), m.p. 139—140° (not const.); hydrolysis with 3·7% HCl at 100° (bath) affords 2-methyl-*l*-rhamnose (II) [*l*-rhamnose-*p*-nitrophenylsazone, new m.p. 209—211° (decomp.)], not readily attacked by $\text{Br-H}_2\text{O}$. Neither (I) nor (II) is identical with digit-*alose*, which must be either 2-methyl-*d*-gulomethyl-*alose* or *l*-altromethyl-*alose*. (II) and 50% HNO_3 at room temp., then HCl-MeOH at 100°, followed by $\text{NH}_2\text{Me-MeOH}$, give *l*-arabomethoxyglutardimethylamide, m.p. 204—205°, $[\alpha]_D^{25} + 71^\circ$ in H_2O . Rhamnal diacetate and $\text{BzO}_2\text{H-CHCl}_3$ at 0° give rhamnose or *epirhamnose* (probably) 3:4-diacetate 1-benzoate, m.p. 193°, $[\alpha]_D^{25} - 15\cdot2^\circ$ in CHCl_3 . The general theory of Pigman and Isbell (A., 1937, II, 444) is supported. A. T. P.

Action of mercury salts on acetohalogeno-sugars. XIII. Synthesis of isoprimerose [6- α -*d*-xylosido-*d*-glucose], the α -isomeride of primerose, and their derivatives. G. ZEMPLÉN and R. BOGNÁR (Ber., 1939, 72, [B], 1160—1167; cf. A., 1939, II, 99).—Treatment of acetobromoxylose and 1-chloroglucose triacetate with an insufficiency of Hg(OAc)_2 in C_6H_6 affords acetochloroprimerose, m.p. 201—203° (corr.), $[\alpha]_D^{25} + 72\cdot1^\circ$ in CHCl_3 [heptaacetate, m.p. 214° (corr.), $[\alpha]_D^{25} - 18\cdot6^\circ$ in CHCl_3],

and α -acetochloroprimerose (I), m.p. 158—160° (corr.) after softening at 154°, $[\alpha]_D^{25} + 180\cdot6^\circ$ in CHCl_3 . (I) is transformed by Ac_2O and AgOAc at 100° into isoprimerose heptaacetate, (II), m.p. 107—110° (corr.) after softening at 104°, $[\alpha]_D^{25} + 91\cdot8^\circ$ in CHCl_3 (highest observed val.), hydrolysed by NaOMe to isoprimerose (6- α -*d*-xylosido[1:5]-*d*-glucopyranose), m.p. 200·5—201·5° (incipient decomp.) after softening at 198°, $[\alpha]_D^{25} + 151\cdot3^\circ$ to $+121\cdot3^\circ$ (const.) in H_2O during 16 hr. TiBr_4 in EtOH -free CHCl_3 converts (II) into acetobromoisoprimerose, m.p. 155·5—157·5° (corr.) after softening at 149°, $[\alpha]_D^{25} + 186\cdot3^\circ$ in CHCl_3 . Acetochloroprimerose and Ag_2CO_3 in boiling CHCl_3 MeOH yield β -1-methylprimeroside hexaacetate, m.p. 219—220° (corr.), $[\alpha]_D^{25} - 37\cdot0^\circ$ in CHCl_3 . 1- β -Methylisoprimeroside hexaacetate, has m.p. 123—124° (corr.), $[\alpha]_D^{25} + 66\cdot0^\circ$ in CHCl_3 . H. W.

Constituents of Forsythia koreana, Nakai. S. KUNIMINE and S. SUZUKI (J. Pharm. Soc. Japan, 1938, 58, 25—28).—Extraction of the leaves of *F. koreana* with H_2O affords *forsythin* (I), $\text{C}_{27}\text{H}_{34}\text{O}_{11}$, m.p. 181°, hydrolysed by emulsin to glucose and *forsythigenol* (II), $\text{C}_{21}\text{H}_{24}\text{O}_8$, m.p. 134·5°. (II) contains 1 phenolic OH and 3 OMe. Oxidation of (II) by KMnO_4 in COMe_2 yields veratric acid (III) whilst similar oxidation of *forsythigenol Et ether*, m.p. 124°, yields (III) and ethylvanillic acid. *Forsythigenol Me ether* (IV), m.p. 129°, cannot be acetylated by $\text{NaOAc-Ac}_2\text{O}$ or by $\text{C}_6\text{H}_5\text{N-Ac}_2\text{O}$ and does not react with $\text{NH}_2\text{-CO-NH-NH}_2$, NH_2OH , or NHPh-NH_2 . It is unchanged when heated with 5% NaOH-EtOH at 100° and is not reduced by Na-EtOH or catalytically (PtO_2). Hence (I) has probably the partial structure



A. Since nitration of (IV) gives 4-nitroveratrole in addition to *dinitroforsythigenol Me ether* the C attached to the 3:4-dimethoxyphenyl group must be united to O. (IV) therefore appears to be stereoisomeric with eudesmin (V) or pinoresinol Me_2 ether (VI). For the same reasons as those on which the constitution of (V) and (VI) are based the complex $\text{C}_{14}\text{H}_{18}\text{O}_2$ of (IV) is regarded as a condensed tetrahydrofuran ring. Reasons are advanced for considering (II) to be identical with phyllygenin and for regarding the glucoside obtained by Eykmann from *F. suspensa*, Vahl, which is identical with or closely related to phyllyrin, as identical with (I). H. W.

Testosterone glucoside. E. RABALD and H. DIETRICH (Z. physiol. Chem., 1939, 259, 251—252).—Testosterone (I) with Ag_2O and acetobromoglucose in Et_2O for 48 hr. yields testosterone glucoside tetraacetate, m.p. 165—166°, hydrolysed with Ba(OMe)_2 to the free glucoside, m.p. 213—214°. J. N. A.

Polysaccharides. XXXI. Constitution of wheat starch and horse-chestnut starch. E. L. HIRST and G. T. YOUNG (J.C.S., 1939, 951—955).—Wheat starch on repeated methylation with $\text{Me}_2\text{SO-NaOH}$ in N_2 , followed by fractional pptn. with light petroleum from CHCl_3 , yields four methylated starches, all having $[\alpha]_D^{25} + 207\text{—}208^\circ$ in CHCl_3 , and

OMe = 42.7–45.5%, but with apparent mol. wts. of 300,000, 300,000, 290,000, and 170,000 (calc. on Staudinger's equation, based on η in *m*-cresol). Hydrolysis of these by 1% MeOH-HCl and determination of the tetramethyl-methylglucoside shows that all four fractions consist of 24–26 glucopyranose units linked in the 1:4 position. Horse-chestnut starch, similarly treated, gives methylated starches with $[\alpha]_D^{20} +204$ – 205° in CHCl_3 , OMe 43.8–43.9%, and apparent mol. wts. 700,000, 650,000, and 430,000. The methylated starch (mol. wt. 700,000) of highest η is shown by the "end-group assay" method to consist of 28 glucopyranose units linked in the 1:4 position.

J. D. R.

Enhancement of parallelism of micelles in natural cellulose. (A cellulose preparation with the highest possible degree of orientation.) T. KUBO (Naturwiss., 1939, 27, 278–279).—X-Ray investigations show that on heating hydrocellulose or compounds derived from it, *e.g.*, alkali-celluloses and diamino-celluloses, with some polar org. liquids, *e.g.*, glycerol, to 250° , a considerable increase in the degree of orientation of the crystallites occurs. This has also been observed with purified natural ramie fibre and Na-cellulose I, the fibres being heated with glycerol at 250° for 45 min. It was possible to prepare in this manner a cellulose which gave a specially sharp X-ray diagram, the detail approaching that given by a single crystal.

A. J. M.

Chemical composition of pine bark. H. FRIESE, E. CLOTOFSKI, and R. DÖDERLEIN (Ber., 1939, 72, [B], 1226–1232).—The bark contains C 55%, H 5.89%, OMe $\sim 3\%$, and ash $>1\%$. Exhaustive extraction with COMe_2 removes $\sim 10\%$, leaving a residue of unchanged composition. Treatment of the residue with super-conc. HCl or 66% H_2SO_4 gives $\sim 68\%$ of undissolved matter whilst the solution contains galactose, rhamnose, and xylose; it is uncertain whether glucose is present. The total pentosan content is 28.3%. Sulphoacetylation of the bark gives $\sim 30\%$ of sugars and a H_2O -sol. sulphonic acid (4.66% OMe) which differs from the ligninsulphonic acid from the wood. Digestion with $\text{Ca}(\text{HSO}_3)_2$ causes deep-seated change. Treatment with alkali at 170 – 180° gives an insol. residue (8.7%) with 42.6% C and 6.7% H. By use of Schweitzer's reagent a portion with 44.15% C and 6.9% H can be isolated; this is doubtless a polysaccharide but it is uncertain whether glucose is the fundamental unit. The unsaccharifiable portion of the bark gives a dark brown solution in 4*N*-NaOH at 100° (dissolved portion with 53.2% C and 4.48% H), leaving 20% of residue with 61.4% C and 5.46% H. Oxidation of the bark with HNO_3 gives $\text{H}_2\text{C}_2\text{O}_4$ and an unidentified yellow NO_2 -derivative. Nitration of the extracted bark with Ac_2O - HNO_3 gives a product with total N 5.37% and ester-N 2.84%, thus showing a marked difference from wood in behaviour. The COMe_2 extract is composed mainly of a mixture of free acids and esters from which an alcohol, m.p. 72° , C 80.91%, H 14.14%, mol. wt. 370, is obtained by hydrolysis; it is unsaturated. The acid component has m.p. 70 – 75° and contains 78.07% C and 13.04% H; it is unsaturated and contains OH. The extractives freely sol. in Et_2O but

sparingly sol. in light petroleum contain free acids and esters and yield an alcohol, m.p. 62° (81.36% C and 14.08% H), and acids, m.p. 74° and 66 – 68° respectively. A tannin is also present.

H. W.

Structure of hexamethylenetetramine. Action of chloro-compounds of sulphur on urotropin. M. DOMINKIEWICZ (Arch. Chem. Farm., 1939, 4, 1–7).— $(\text{CH}_2)_6\text{N}_4$ and SCl_2 , S_2Cl_2 , SOCl_2 , or SO_2Cl_2 in CHCl_3 yield *dichloroformin*,

$\text{R}_2 \left(\text{R} = \cdot \text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{NHCl} \right)$, m.p. 193 – 194° . With SCl_2 the *sulphide*, R_2S , and with SOCl_2 , *thionylidiformin*,

$\text{SO} \left(\text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \cdot \right)_2$, m.p. 183 – 185° , are also obtained.

R. T.

Attempted resolution of substituted cyclic ethyleneimines into optically active isomerides. J. MEISENHEIMER and L. H. CHOU (Annalen, 1939, 539, 70–77).—Attempts to prepare optically active N^{III} derivatives containing the N in a strongly strained ring failed, although the strain might be expected to stabilise the asymmetry. 2-Methylethyleneimine, b.p. 61 – $62.5^\circ/728$ mm. (*picrate*, m.p. 110°), gives a *d-camphorate*, m.p. 210° , $[\alpha]_D^{20} +34$ – 69° , recrystallisation of which does not cause resolution; other active salts were oils. $\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ could not be obtained from $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ by MgMeI or from $\text{CN}\cdot\text{CMe}_2\cdot\text{OH}$ by H_2 -PtO₂ in AcOH . $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ (prep. from $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ by MgEtI) is unchanged by HCl at room temp., and at 50° gives oils. $\text{NHBz}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ and SOCl_2 in CHCl_3 give \rightarrow traces of a substance, m.p. 115° . The hydrochloride of $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{OH}$ (I) (prep. in 88% yield by $\text{CH}_2\text{Ph}\cdot\text{MgCl}$) is unchanged by PCl_5 - POCl_3 or SOCl_2 , and with HCl at 100° gives γ -phenyl- β -benzylidene-*n*-propylamine [hydrochloride, m.p. $>250^\circ$; *picrate*, m.p. 218 – 219° (decomp.)]. The N-Bz derivative, m.p. 129 – 130° , of (I) is unchanged by SOCl_2 in CHCl_3 at room temp., and with SOCl_2 (alone) or POCl_3 (alone) at room temp. or hot PCl_5 - PCl_3 or $\text{HBr}\cdot\text{AcOH}$ at 100° gives oils. Attempts to replace the OH of $\text{NH}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ (II) by Cl failed, but the N-Ac derivative (III), m.p. 142 – 143° , thereof with SOCl_2 - CHCl_3 gives *acet*- β -chloro- β -*diphenylethylamide*, m.p. 133 – 135° , converted by hot EtOAc or light petroleum into *acet*- β -*diphenylvinylamide*, m.p. 163° [obtained directly from (III) by hot PCl_5 - POCl_3], and hydrolysed by cold 10% $\text{KOH}\cdot\text{EtOH}$ to (III) or by hot 30% $\text{KOH}\cdot\text{EtOH}$ to (II).

R. S. C.

Action of carbon disulphide on amino-compounds. I. Spectrographic study of some simple dithiocarbamates. K. KANAMARU, T. TAKADA, and T. TANIGUCHI (J. Soc. Chem. Ind. Japan, 1939, 42, 47–50B).—Amines react more readily than alcohols with CS_2 in absence of alkali, giving dithiocarbamic acids. Comparison of their absorption spectra with that of $\text{OPr}\cdot\text{CS}\cdot\text{SNa}$ shows that NH_4 dithiocarbamate, Na propyldithiocarbamate, and the product obtained from glycine, CS_2 , and NH_3 in EtOH contain the group $\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot$. With certain metallic

salts, dithiocarbamates give characteristic ppts. similar to those given by alkyl xanthates. A. Li.

Monoacetoxymethyl phosphate. P. PRATESI (Ber., 1939, 72, [B], 1459—1461).—A solution of Na_2HPO_4 in H_2O is warmed to 45—50° with $\text{CH}_3\text{Cl}\cdot\text{OAc}$ (I) and so much 2N-NaOH that the solution is always just alkaline to litmus. When reaction is complete any remaining (I) is removed by Et_2O , after which CaCl_2 and 2N-NaOH (just red to phenolphthalein) are added. The pptd. $\text{Ca}_3(\text{PO}_4)_2$ is removed and *Ca acetoxymethyl phosphate*, $\text{OAc}\cdot\text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{Ca}$, is pptd. from the filtrate by EtOH . It does not give a ppt. with cold AgNO_3 or an immediate ppt. with NH_3 . It reduces hot aq. AgNO_3 , loses CH_2O when boiled with H_2O , and gives a positive cacodyl reaction after hydrolysis. It is much more rapidly hydrolysed by taka-phosphatase at p_H 5.2 and 20° than by chemicals under like conditions. H. W.

New method of phosphorylation; 1-glucosyl-phosphate. L. ZERVAS (Naturwiss., 1939, 27, 317).—A suitable org. halogen compound is treated with $\text{Ag}(\text{CH}_2\text{Ph})_2\text{PO}_4$ (I), and the resulting ester dissolved in PhMe is reduced with H_2 (Pd). From bromoglucose tetra-acetate and (I) is obtained *glucose 2:3:4:6-tetra-acetate 1-dibenzyl phosphate*, m.p. 79°, $[\alpha]_D^{20} -9^\circ$ in CHCl_3 . W. O. K.

Action of boric esters in hydroxyl derivatives. H. WUYTS and (MLLE.) A. DUQUESNE (Bull. Soc. chim. Belg., 1939, 48, 77—93).—Excess of $\text{B}(\text{OPr}^a)_3$ (I) and the corresponding alcohol at <190° afford *isoamyl*, b.p. 131.8—133°/12 mm., *sec.-amyl*, b.p. 109.8—114°/12 mm., *benzyl*, b.p. 180.4—189.8°/3 mm., *cyclohexyl*, b.p. 137.8—141.2°/1.5 mm., *geranyl*, *bornyl*, m.p. 226.4°, $[\alpha]_D^{20} +32.42^\circ$ in C_6H_6 , *dimethyl-n-butyl*, b.p. 102.4—117.2°/1 mm., and *glycol borate*, b.p. 91.8—92.3°/10 mm. Excess of (I) and the respective phenol give *phenyl*, m.p. 38—40°, b.p. 141.6—148°/1.5 mm., *m-tolyl*, m.p. 54.2°, b.p. 185—195°/3 mm., and *guaiacyl borate* (reaction at 203°), m.p. 101—101.8°, b.p. 200°/2 mm. $p\text{-C}_6\text{H}_4(\text{OH})_2$, $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}^a$ give impure products; $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}^a$ does not react. (I) and $o\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ give EtCHO , Pr^aOH , and a product containing B, decomposed by H_2O vapour to (?) $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot[\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2]_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ (mechanism suggested), sol. in Et_2O , and a product, $\text{C}_{14}\text{H}_{14}\text{O}_3$, insol. in Et_2O . Borates from glucose (at 190°, 5 OH are attacked) and sucrose (at 180° or 215°, corresponds with ethers of 3 or 4 OH respectively) are not obtained pure. Cellulose does not react with (I). A. T. P.

Primary compounds in Grignard reactions. P. PFEIFFER and H. BLANK (J. pr. Chem., 1939, [ii], 153, 242—256).—When MgEtBr and COPh_2 in mol. ratio 1:1 are mixed in abs. Et_2O at 0° a dirty white ppt. is formed which so readily passes into an oil that it cannot be analysed. It is doubtless $\text{CPh}_2\text{O}\cdots\text{MgEtBr}$ since it affords COPh_2 in good yield when decomposed by H_2O . With excess of the reagent (1:2) the product is hydrolysed to $\text{CPh}_2\text{Et}\cdot\text{OH}$. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ and MgEtBr (1:0.5 or 1:1) at 0° yield $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{CO}\cdots\text{MgEtBr}$ from which the ketone is regenerated even if the mixture has been

heated at 100° for 5 hr. If the mol. ratio is 1:2 or 1:3 the product contains more Grignard compound but is indefinite in composition. Carbinol in addition to ketone is obtained only from the product given by the reactants in the 1:3 ratio and appears predominately if the ratio is 1:4. Similar results are recorded with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$, the mol. ratio 1:3 being essential for the production of ketone. The mol. compound $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{CO}\cdots\text{MgEtBr}$ from $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{-}p)_2$ is formed with the components in the ratio 1:1, 1:2, or 1:3, and gives exclusively ketone when treated with H_2O even after it has been heated at 100° for 5 hr. If the components are in the ratio 1:4, the product of the decomp. is di- $\alpha\alpha$ -tetramethyldiaminodiphenyl- Δ^a -propene, m.p. 99—100°. *Phenyl-p-dimethylaminophenylethylcarbinol*, m.p. 74°, and *phenyl-p-aminophenyl-n-butylcarbinol*, m.p. 105—106°, appear new. H. W.

Apparatus for reactions of organo-magnesium compounds. R. BOUSSET (Bull. Soc. chim., 1939, [v], 6, 988—990).—An illustrated description of apparatus which may be used for reactions in absence of air. A. T. P.

Mercuri-organic allyl derivatives. M. DOMINI-KIEWICZ and M. KIJEWKA (Arch. Chem. Farm., 1939, 4, 8—22).—*o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in EtOH and $\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ heated with K_2CO_3 (3 hr. at the b.p.) yield *allyl o*- or *p*-*allylaminobenzoate*, oils, from which *o*-, m.p. 215° (decomp.), or *p*-*allylaminobenzoic acid*, m.p. 128—129° (lit. 144—146°), is obtained. These acids with $\text{Hg}(\text{OAc})_2$ in MeOH give *o*-, m.p. 215° (decomp.), or *p*-(γ -*acelomercuri*- β -*methoxypropyl-amino*)benzoic acid, from which the corresponding *OH*-*Hg*-compounds are obtained by the action of NaOH . Diallylacetyl chloride (I) and *o*- or *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ yield *o*-, m.p. 108—109°, or *p*-*diallylacetamidobenzoic acid*, m.p. 215.5—216°, which with $\text{Hg}(\text{OAc})_2$ give respectively *o*- and *p*-($\gamma\gamma'$ -*diacetomercuri*- $\beta\beta'$ -*dimethoxydipropylamino*)benzoic acid, decomp. at 185—193°, converted by NaOH into the corresponding *OH*-*Hg*-compounds, m.p. 213—215° (decomp.) and >360°, respectively. $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$ and (I) in PhMe (3 hr. at the b.p.) yield *phthal-diallylacetamide*, m.p. 230—232°, which with $\text{Hg}(\text{OAc})_2$ gives *phthal- $\gamma\gamma'$ -diacetomercuri- $\beta\beta'$ -dimethoxypropyl-acetamide*, m.p. 149° (decomp.), and this with NaOH affords the corresponding *dihydrozymercuri*-compound. R. T.

Isomerisation of polymethylene hydrocarbons in presence of aluminium chloride. II. Isomerisation of methylcyclopentane. M. B. TUROVA-POLAK and N. B. BARANOVSKAJA (J. Gen. Chem. Russ., 1939, 9, 429—431).—The equilibrium methylcyclopentane (16%) \rightleftharpoons cyclohexane (84%) is established in presence of AlCl_3 at 100°. R. T.

Isomerisation of polymethylene hydrocarbons in presence of aluminium chloride. I. Propylcyclopentane. M. B. TUROVA-POLAK and O. I. POLJAKOVA (J. Gen. Chem. Russ., 1939, 9, 233—238).—The product obtained from propylcyclopentane and AlCl_3 at 145° consists of 1:3- and 1:4-dimethylcyclohexane (91.8%), cyclopentane compounds (6.4%), and paraffin hydrocarbons (1.8%). R. T.

Hydrocarbons of the cyclopentane series. H. SUDA and A. GEMASSMER (Ber., 1939, 72, [B], 1168—1173).—Ring contraction of cyclohexane hydrocarbons, the Friedel-Crafts and Fittig-Wurtz reactions are not suitable for the production of pure cyclopentane hydrocarbons. Under defined conditions cyclopentanones are converted by Grignard's reagents into cyclopentanol, dehydrated by KHSO_4 to cyclopentenenes, which are hydrogenated (Pt sponge in AcOH) to cyclopentanes. Use of Mg cyclopentyl chlorides is impracticable on account of their very marked reducing properties. The following data are new or revised: *octadecylcyclopentene*, b.p. 173—174°/3 mm., m.p. 19°, and *-pentane*, b.p. 175—176°/3 mm., m.p. 23°; *1-methyl-3-octadecylcyclopentene*, b.p. 179°/2 mm., m.p. 18°, and *-pentane*, b.p. 161—162°/0.001 mm., m.p. 21.5°; *2-cyclopentyl-1-octadecylcyclopentene*, b.p. 196—197°/0.001 mm., m.p. ~5—10°, and *-pentane*, b.p. 197°/0.001 mm., m.p. ~18°; *2:5-dicyclopentyl-1-octadecylcyclopentene*, b.p. 225—227°/0.001 mm.; *octadecylcyclohexene*, b.p. 179—180°/3 mm., m.p. 20°, and *-hexane*, b.p. 180°/3 mm., m.p. 23.5°; *octadecylbenzene* (from C_6H_6 and stearyl chloride with subsequent reduction), b.p. 183°/3 mm., m.p. 30° (from C_6H_6 and octadecyl chloride, Friedel-Crafts), b.p. 180—181°/3 mm., m.p. 25—26°. H. W.

Hydrogenation of ethylbenzene under pressure. P. V. PUTSCHKOV and A. F. NIKOLAEVA (J. Gen. Chem. Russ., 1939, 2, 280—284).—PhEt and H_2 at 400°/90 atm. (MoS_2 catalyst) yield chiefly cyclopentane hydrocarbons, together with C_2H_6 , C_6H_6 , cyclohexane, and ethylcyclohexane. R. T.

Attempts at asymmetric syntheses. R. BOUSSET (Bull. Soc. chim., 1939, [v], 6, 983—986).—*p*-Methylcyclohexanol (I) is incompletely dehydrated by optically active camphoric or dicinnamoyltartaric anhydride to an inactive hydrocarbon. Quant. dehydration of (I) (1 mol.) by camphor-10-sulphonic acid (0.1 mol.) or its chloride at 120° or 135—137°, respectively, gives inactive 1-methyl- Δ^3 -cyclohexene. A. T. P.

1:4-Diaryl- $\Delta^{1:3}$ -cyclopentadienes. N. L. DRAKE and J. R. ADAMS, jun. (J. Amer. Chem. Soc., 1939, 61, 1326—1329).— $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I), COPhMe , and NaOEt in C_6H_6 at 40° give 1:3-diphenyl- $\Delta^{1:3}$ -cyclopentadiene-4-carboxylic acid, non-fluorescent, m.p. 157—158° (extractable as Na salt with cold H_2O), which in aq. NaOH at ~60° loses CO_2 and by migration of H yields fluorescent 1:4-diphenyl- $\Delta^{1:3}$ -cyclopentadiene (II), m.p. 158—158.5° [picrate, m.p. 145—146° (decomp.); $\text{C}_6\text{H}_5(\text{NO}_2)_3$ derivative, m.p. 151—152° (decomp.); maleic anhydride adduct, m.p. 154°]. The structure of (II) is proved by hydrogenation (Pd-C) in EtOH to 1:3-diphenylcyclopentane, b.p. 140—141°/3 mm., and ozonolysis to CH_2Bz_2 and $(\text{CHO})_2$ [*p*-nitrophenylosazone, m.p. 306—307° (decomp.)], and is confirmed by prep. of 1-phenyl-4-*p*-tolyl- $\Delta^{1:3}$ -cyclopentadiene, m.p. 153—153.5° [$\text{C}_6\text{H}_5(\text{NO}_2)_3$ derivative, m.p. 145—146° (decomp.)]; maleic anhydride adduct, m.p. 146—146.5°, from (I) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ or *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ and COPhMe , which would give different compounds if the 1:3-diaryl structure were retained. 1-Phenyl-4-*p*-xenyl- $\Delta^{1:3}$ -cyclopenta-

diene, m.p. 217—218° (decomp.), is similarly prepared. The "1:3-diphenyl- $\Delta^{1:3}$ -cyclopentadiene" of Borsche et al. (A., 1908, i, 150) was really (II). R. S. C.

Addition of hydrogen chloride to propenylbenzene. S. P. LAGEREV and A. A. SCHAMSCHURIN (J. Gen. Chem. Russ., 1939, 9, 199—202).— $\text{CHPhEt}\cdot\text{OH}$ in Et_2O and HCl yield α -chloropropylbenzene (I), b.p. 77—78°/8 mm. $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{OH}$ similarly affords β -chloropropylbenzene (II), b.p. 94—95°/9 mm. (I) and (II) with KOH in EtOH yield $\text{CHPh}\cdot\text{CHMe}$, which with HCl in Et_2O gives (I), and with Br in CHCl_3 gives $\alpha\beta$ -dibromopropylbenzene, m.p. 67°. It is concluded that in the addition of HCl, Cl has a greater affinity for the C attached to Ph than to Me. R. T.

β -Nitroethylbenzene. S. KANAO (J. Pharm. Soc. Japan, 1938, 58, 62—65).— α -Chloro- β -phenylpropionic acid (I), b.p. 176—177°/18 mm., $[\alpha]_D^{20} + 10.19^\circ$ in C_6H_6 (Et ester, b.p. 134—134.5°/13 mm., $[\alpha]_D^{20} + 16.64^\circ$ in EtOH), obtained from crude *l*-phenylalanine and NaNO_2 in aq. HCl, is converted by $\text{MeOH}\cdot\text{NaOMe}$ into cinnamic acid and by NH_2Ph into *N*-phenylphenylalanine, m.p. 173—174°. Steam-distillation of (I) (as Na salt) + NaNO_2 gives 11% of β -nitroethylbenzene, b.p. 249—251° (partial decomp.)/763 mm. (Na salt of *aci*-form), reduced (H_2 , PtO_2 , EtOH) to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$. H. B.

Condensation of methyl chloro- and bromomethyl ether and aromatic compounds. G. VAVON, J. BOLLE, and J. CALIN (Bull. Soc. chim., 1939, [v], 6, 1025—1033).—Substituents, e.g., Me, Et, Pr, OMe, OPr, usually aid reaction (exceptions given) between $\text{CH}_2\text{Cl}\cdot\text{OMe}$ (I) and aromatic compounds, whilst halogen, CH_2Cl , CO_2H , NO_2 impede it. Compared with C_6H_6 (= 1), the rates for PhMe, *m*-xylene, *s*- $\text{C}_6\text{H}_3\text{Me}_3$, PhOMe, and 3:5:1- $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{OMe}$ are 3, 24, 600, 1300, and >100,000, respectively; the rates for PhNO₂ and nitromesitylene are too small to measure. $\text{CH}_2\text{Br}\cdot\text{OMe}$ (II) reacts 10 times as fast as does (I). Relative speeds of hydrogenation of the CH_2Cl to Me derivatives are given. Condensation of (I) and *s*- $\text{C}_6\text{H}_3\text{Me}_3$ or PhOMe occurs more rapidly in $\text{AcOH}\cdot\text{HCO}_2\text{H}$ and $\text{CHCl}_2\cdot\text{CO}_2\text{H}$ than in AcOH alone. PhMe and (I) (modified prep.) give *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Cl}$; *o*- and *m*-xylene afford 3:4:1- and 2:4:1- $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CH}_2\text{Cl}$, respectively; ψ -cumene gives 2:4:5:1- $\text{C}_6\text{H}_2\text{Me}_4\cdot\text{CH}_2\text{Cl}$ + a little $(\text{CH}_2\text{Cl})_2$ derivative, m.p. 85°, and di- ψ -cumylmethane. *s*- $\text{C}_6\text{H}_3\text{Me}_3$ gives 2:4:6:1- $\text{C}_6\text{H}_2\text{Me}_4\cdot\text{CH}_2\text{Cl}$ [(II) gives the bromide], hydrogenated (Pt-black in EtOH) to 1:2:4:6- $\text{C}_6\text{H}_2\text{Me}_4$; further successive chloromethylation and hydrogenation, which affords a new method of introducing Me, gives 2:3:4:6:1- $\text{C}_6\text{HMe}_5\cdot\text{CH}_2\text{Cl}$, C_6HMe_5 , $\text{C}_6\text{Me}_5\cdot\text{CH}_2\text{Cl}$, and thence C_6Me_6 . C_{10}H_8 gives 1- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Cl}$ [(II) gives the bromide], and thence 1- $\text{C}_{10}\text{H}_7\text{Me}$ and 1:4- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{CH}_2\text{Cl}$. Tetrahydronaphthalene gives the 2-(+ some 1-) CH_2Cl derivative. PhOMe yields *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ and thence *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$, 1:4:2- $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CH}_2\text{Cl}$, 2:4:1- $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{OMe}$, $\text{C}_6\text{H}_2\text{Me}_4\cdot\text{OMe}$ (2:4:6:1 + 2:4:5:1), $\text{C}_6\text{HMe}_4\cdot\text{OMe}$, and $\text{C}_6\text{Me}_5\cdot\text{OMe}$. *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OMe}$ gives the 2- CH_2Cl derivative, and thence 4:2:1- $\text{C}_6\text{H}_3\text{BrMe}\cdot\text{OMe}$, 1:4:6:2- $\text{OMe}\cdot\text{C}_6\text{H}_2\text{BrMe}\cdot\text{CH}_2\text{Cl}$, and 4:2:6:1-

$C_6H_5BrMe_2\cdot OMe$. $p\text{-}OMe\cdot C_6H_4\cdot CO_2Et$ and (II) give 1 : 4 : 3- $CO_2Et\cdot C_6H_3(OMe)\cdot CH_2Br$, and thence 1 : 3 : 4- $CO_2Et\cdot C_6H_3Me\cdot OMe$. A. T. P.

Hydrogen fluoride as a condensing agent. VI. Alkylation of benzene with compounds containing an "allylic" group. J. H. SIMONS and S. ARCHER (J. Amer. Chem. Soc., 1939, 61, 1521—1522; cf. A., 1939, II, 54).— C_6H_6 , CH_3PhCl , and HF at 100° give 56% of CH_2Ph_2 , which precludes this type of reaction proceeding by way of an olefine.

$CHPh\cdot CH\cdot CO_2H$, C_6H_6 (excess), and HF give 53% of $CHPh_2\cdot CH_2\cdot CO_2H$. $CH_3\cdot CH\cdot CH_2\cdot OH$, C_6H_6 , and HF at 100° give 11—20% of $CH_2Ph\cdot CH\cdot CH_2$ (I) (*Br*-derivative *dibromide*, m.p. 124.5—125°) and 12—7.5% of $CH_2Ph\cdot CHPhMe$ (II); H_2SO_4 leads to 32% of (II). C_6H_6 , (I), and HF at 0° give 62.5% of (II). R. S. C.

Stabilisation of styrene.—See B., 1939, 696.

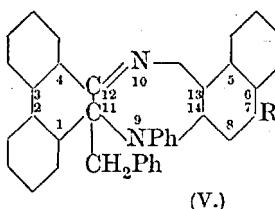
Oxidation of α -methylstyrene.—See B., 1939, 696.

Isomerisation of allene hydrocarbons in presence of silicates. VIII. Isomerisation of α -phenyl- Δ^2 -butinene and α -phenyl- Δ^2 -butadiene. J. M. SLOBODIN (J. Gen. Chem. Russ., 1939, 9, 272—276).— $CH_2Ph\cdot CH_2\cdot C\equiv CH$ (I) is very stable in presence of floridin at 250°, only small amounts of $CH_2Ph\cdot CH\cdot C\equiv CH_2$ (II) being found in the condensate. $CHPh\cdot CH\cdot CH\cdot CH_2$ (III) yields chiefly (I) with floridin at 290°. The processes are represented (I) \rightleftharpoons (II) \rightleftharpoons (III), the stability of the products falling in the order given. R. T.

Low-temperature dehydrogenation of hydroaromatic rings. R. T. ARNOLD and C. J. COLLINS (J. Amer. Chem. Soc., 1939, 61, 1407—1408).—Chloranil in boiling xylene is an efficient, but mild, dehydrogenating agent for many hydroaromatic compounds. A 5—10% excess of the quinone is used, owing to oxidation of the solvent. Thus, 1 : 2 : 3 : 4-tetrahydrophenanthrene gives 56% of phenanthrene (22 hr.), 9 : 10-dihydroanthracene gives 63% of anthracene (33 hr.), phenylcyclohexene gives 52% of Ph_2 (4 hr.), 6-methoxyflavanone gives 60—70% of 6-methoxyflavone (15 hr.), and 1 : 2 : 3 : 4-tetrahydronaphthalene gives (?) 100% of $C_{10}H_8$ (14 hr.). Decahydronaphthalene gives a mixture, and methylcyclohexene does not react. R. S. C.

Anthracene and phenazine derivatives. J. MEISENHEIMER and F. W. DITT (Annalen, 1939, 539, 57—69).—2 : 3 : 6 : 1- $CO_2H\cdot C_6H_4Cl_2\cdot CO\cdot C_6H_3Me_2$ -1 : 2 : 5 [prep. in 69% yield from 3 : 6 : 1 : 2- $C_6H_2Cl_2(CO_2)O$, *p*-xylene, and $AlCl_3$] with H_3BO_3 and 10% oleum at 120° gives 88% of 5 : 8-dichloro-1 : 4-dimethylantraquinone, decomp. $\sim 300^\circ$ (lit. m.p. 244°), reduced by granulated Zn and a little HCl in AcOH to 5 : 8-dichloro-1 : 4-dimethyl-9-anthrone (84%), m.p. 221° (cf. Barnett, A., 1932, 1135), which with an excess of $CH_2Ph\cdot MgCl$ in Et_2O at -10° to -15° gives 76% of 5 : 8-dichloro-9-hydroxy-9-benzyl-1 : 4-dimethyl-9 : 10-dihydroanthracene (I), m.p. 166°. With hot $HCl\text{-}AcOH$, (I) gives 5 : 8-dichloro-1 : 4-dimethylanthrane, m.p. 224—228° (*loc. cit.*, 230°) (the CH_2Ph being lost as $CH_2Ph\cdot OH$), and (? *cis*- and *trans*-)forms, m.p. 182—183° (II) and 250° (decomp.),

of 5 : 8-dichloro-9-benzylidene-1 : 4-dimethyl-9 : 10-dihydroanthracene. However, with KOH in hot xylene, (I) gives 53% of 5 : 8-dichloro-9-benzyl-1 : 4-dimethylanthrane (III), m.p. 141—142° (no picrate), and some (II); (III) is an intermediate, since it is converted into (II) by KOH in xylene. With $SOCl_2$, (I) gives 5 : 8 : 9-trichloro-9-benzyl-1 : 4-dimethyl-9 : 10-dihydroanthracene, m.p. 170° (decomp.), which is resistant to KOH or $NPhEt_2$, but with hot ROH yields 5 : 8-dichloro-9-ethoxy-, m.p. 170—171°, and -9-methoxy-9-benzyl-1 : 4-dimethyl-9 : 10-dihydroanthracene, m.p. 165°. Naphthoflavinduline chloride (IV) (prep. from 1 : 2- $NH_2\cdot C_{10}H_6\cdot NHPh$, phenanthraquinone, and HCl in AcOH) (picrate, decomp. $> 270^\circ$) and $CH_2Ph\cdot MgCl$ in Et_2O give 9-phenyl-11-benzyl-9 : 11- (V) ($R = H$), yellow, decomp. 186°, and 9-phenyl-10-benzyl-9 : 10-dihydro-1 : 2 : 3 : 4 : 5 : 6-tribenzophenazine, +0.5MeOH, colourless, decomp. 186° (insufficiently basic to form salts with optically active acids). Phenanthrophenyl rosinduline chloride [prep. from (IV) by NH_2Ph ; $NHEt_2$ gives non-cryst. products] and $CH_2Ph\cdot MgCl$ in $Et_2O\text{-}N_2$ give similarly 7-anilino-9-phenyl-11-benzyl-9 : 11-dihydro- (V) ($R = NHPh$), decomp. 186°, and 7-anilino-9-phenyl-10-benzyl-9 : 10-dihydro-1 : 2 : 3 : 4 : 5 : 6-tribenzophenazine, decomp. 186° (does not afford a cryst. bromocamphorsulphonate). R. S. C.



(V.)

($R = NHPh$), decomp. 186°, and 7-anilino-9-phenyl-10-benzyl-9 : 10-dihydro-1 : 2 : 3 : 4 : 5 : 6-tribenzophenazine, decomp. 186° (does not afford a cryst. bromocamphorsulphonate). R. S. C.

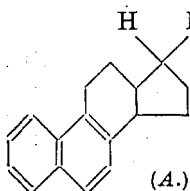
Synthesis of phenanthrene derivatives. II. 9 : 10-Disubstituted hydrocarbons. C. K. BRADSHAW and R. ROSHER (J. Amer. Chem. Soc., 1939, 61, 1524—1525; cf. A., 1939, II, 55).—The crude carbinals, $o\text{-}C_6H_4Ph\cdot CPh(OH)\cdot CHR\cdot OPh$ ($R = Et$, m.p. 83—91°), obtained from $o\text{-}C_6H_4Ph\cdot MgI$ and $COPh\cdot CHR\cdot OPh$ in C_6H_6 , give excellent over-all yields of 9 : 10-disubstituted phenanthrenes when heated with conc. HBr and AcOH. Thus are obtained 9 : 10-diphenyl-, m.p. 234°, 9-phenyl-10-methyl-, m.p. 99—100°, and 9-phenyl-10-ethyl-phenanthrene, m.p. 161°. $COPh\cdot CHEtBr$, b.p. 168—170°/19 mm., $PhOH$, and K_2CO_3 in $COMe_2$ give 66% of α -phenoxybutyrophenone, m.p. 70°. $COPh\cdot CHMeBr$, b.p. 141°/18—20 mm., gives similarly 62% of α -phenoxypropionophenone, m.p. 79—80°. R. S. C.

Substitution reactions of 1 : 2-benzanthracene. A. DANSI and C. FERRI (Gazzetta, 1939, 69, 195—198).—1 : 2-Benzanthracene (I) and $CH_2Cl\cdot CO_2Et$ with Cu powder at 210° give the *Et* ester, m.p. 85°, of 1 : 2-benzanthranyl-10-acetic acid, m.p. 273° (*Ag* and *Na* salts), which at 300° loses CO_2 , giving 10-methyl-1 : 2-benzanthracene. With $AlCl_3$ in $PhNO_2$, followed by $AcCl$, (I) gives the 10-Ac derivative, m.p. 104—105° (cf. Cook *et al.*, A., 1933, 1299), which with boiling 6% NaOCl gives 10-trichloroacetyl-1 : 2-benzanthracene, m.p. 156°. E. W. W.

Thermolysis of cholesteryl chloride. E. BERGMANN and F. BERGMANN (J.C.S., 1939, 1019—1021; cf. A., 1936, 600).—Migration of the $C_{13}\text{-Me}$ in dehydrogenative conversion of steroids into 3'-methylcyclopentenophenanthrene (I) occurs during thermal decomp. of steroid mols. and is not necessarily con-

nected with dehydrogenation. The compound $C_{19}H_{30}$ (II) (*loc. cit.*) is a tetracyclic hydrocarbon with one double linking; hydrogenation (Pd-BaSO₄ reactivated several times by air; BuOH) gives a hydrocarbon, $C_{19}H_{32}$, b.p. 169–174°/1 mm., and a product, $C_{19}H_{20}O_4$, m.p. 246.5° (catalytic oxidation). (II) and Se at 300–320° (sealed tube) give (I),

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene (III), a hydrocarbon, $C_{18}H_{20}$, b.p. 180–190°/0.18 mm. (probably *A* or an isomeride), and a hydrocarbon, $C_{14}H_{16}$ or $C_{15}H_{18}$, b.p. 130°/0.6 mm. The hydrocarbon, $C_{15}H_{22}$ (*loc. cit.*) (formula and mechanism of formation are suggested) and Se (275–300°) give (III) and phenanthrene. The substance, $C_{15}H_{12}$, m.p. 91–92°, obtained from cholesterol by Fischer *et al.* (A., 1926, 399) is probably 9-methylphenanthrene (IV) and the substance, $C_{18}H_{14}$, m.p. 203° (Fischer), is impure chrysene. (IV), prepared from phenanthrene-9-aldehyde semicarbazone and NaOEt at 200°, has m.p. 99.5°; its picrate, m.p. 153°, does not depress the m.p. (145°) of phenanthrene picrate. A. T. P.



Action of acid clay on sterols. VI. Formation of phenylcholestene from cholesterol methyl ether. T. KAWASAKI and Z. YAMAMURA (J. Pharm. Soc. Japan, 1938, 58, 159–161).—Cholesterol Me ether (I) and acid clay (II) in boiling C_6H_6 give 3-phenyl- Δ^5 -cholestene, m.p. 153° (dibromide, m.p. 53–68°) [reduced (H_2 , Pt-black) to 3-cyclohexylcholestane, m.p. 156°], together with material, m.p. 253°, and oil. The OMe of (I) is eliminated as MeOH. Cholesterol Me ether and (II) in boiling C_6H_6 similarly afford phenylcholestane, m.p. 113–126°, but (I) and (II) in boiling C_6H_{14} give an oil and a substance, m.p. 280°. H. B.

5:11-Diphenyl-6:12-didiphenylnaphthacene: its photo-oxide. D. DUVEEN and A. WILLEMART (Compt. rend., 1939, 208, 1587–1588; cf. A., 1939, II, 55).— $C_6H_5Ph \cdot C \equiv C \cdot MgBr$ with $COPh_2$ gives $\alpha\alpha$ -diphenyl- γ -diphenylpropargyl alcohol, m.p. 133–134°, converted by PCl_3 into the chloride (unstable), which when heated gives 5:11-diphenyl-6:12-didiphenylnaphthacene, m.p. 317° (block). This is thermochromic in the solid state and in solution is strongly fluorescent. When insolated it forms a photo-oxide, $C_{54}H_{36}O_2$, which liberates 70% of its O_2 when heated. J. L. D.

Action of sulphur on analogues of anthracene. C. MARSHALK (Bull. Soc. chim., 1939, [v], 6, 1122–1125).—6:17-Dihydroheptacene, 5:16-dihydrohexacene, 6:13-dihydropentacene (I), and 5:12-dihydronaphthacene (II) afford cryst. products (A) with S in boiling $C_6H_5Cl_3$ or $PhNO_2$. Dehydrogenation occurs first; e.g., (I) or (II) gives pentacene (III) or naphthacene respectively, as the latter compounds react similarly with S. (A) are also formed in absence of air, e.g., in CO_2 . The product from (I) corresponds with 6 atoms of S to 1 mol. of (III), and has m.p. >450°. A. T. P.

Catalytic activity of intermetallic compounds in the gas-phase reduction of nitrobenzene.—See A., 1939, I, 424.

Steric influences on the phenomenon of resonance.—See A., 1939, I, 405.

2-Nitro- and 2-amino-*p*-cymene.—See B., 1939, 694.

Chromoisomerism of diphenylamine derivatives. E. HERTEL and M. SCHINZEL (Z. Elektrochem., 1939, 45, 401–404).—From measurements of the absorption spectra of solutions in EtOH it is concluded that the 4'-substitution products of 2:4:6-trinitrodiphenylamine (I) can exist in two forms, *A* and *B*. In the yellow or orange-red form *A* the absorption band at ~3700 Å. is scarcely affected by the substituent group, but in the red form *B* the 4'-groups act as chromophores, causing a broadening of the absorption band and a shift of its max. towards longer λ . With 4'-NH₂ or -NEt₂ the shift in the absorption band disappears on addition of HCl. Form *A* is stabilised by 4'-NO₂ or -Br, so that form *B* of these compounds cannot be obtained. Form *B* is stabilised by Me < OMe < NH₂ < NMe₂ < NEt₂. With (I) itself and its 4'-Me derivative both forms can coexist in equilibrium. The two forms of the 4'-OMe-derivative, however, do not pass into one another in solution. It is concluded that the difference between the forms lies essentially in the (electromeric) state of the central N atom. 4'-Diethylamino-, m.p. 157°, 4'-dimethylamino-, m.p. 180°, 4'-amino-, m.p. 189.5°, 4'-methoxy-, m.p. 170° (red form) and 162° (yellow form), 4'-methyl-, both forms, m.p. 151°, and 4'-bromo-2:4:6-trinitrodiphenylamine, m.p. 181°, are prepared (cf. A., 1930, 1574) from 1:2:4:6-OMe- $C_6H_2(NO_2)_3$ and the appropriate p - $C_6H_4R \cdot NH_2$. Picryl chloride and p -NH₂- $C_6H_4 \cdot NO_2$ in COMe₂ yield 2:4:6:4'-tetranitrodiphenylamine, m.p. 219°. J. W. S.

Molecular compounds of carbamide derivatives. I. E. OCHIAI and S. KUROYANAGI (J. Pharm. Soc. Japan, 1938, 58, 263–266).—F.p. diagrams show that NH₂·CO·NHMe and p -NO₂· C_6H_4 ·OH (I) form a 1:1 compound, m.p. 90° (isolable from components in COMe₂), whilst NH₂·CO·NHPh (II) and m - C_6H_4 (OH)₂ give a 1:5 and a 1:1 compound, m.p. 111.5° (isolable from components in C_6H_6 -EtOAc). (II) and (I) also form a 1:1 compound. Compound formation does not occur between (II) and β - $C_{10}H_7$ ·OH or aminopyrine (III) and between NH₂·CO·NH·COPr and (I), (III), m - C_6H_4 (OH)₂, β - $C_{10}H_7$ ·OH, or anisic acid. H. B.

Dulcine. V. Transformations of dulcine. VI. Pyrolysis of chloroacetyl- and of monobenzoyl-dulcine. C. ALBERTI (Gazzetta, 1939, 69, 150–162, 162–166).—V. The (MgBr)₂ derivative of dulcine (p -phenetylcarbamide) (I) with $CH_2Cl \cdot COCl$ gives 1- p -phenethylhydantoin (II), m.p. 201–202°, which with boiling dil. Ba(OH)₂ gives N - p -phenethylcarbamido- N -acetic acid, m.p. 179–180° (salts described). The MgBr derivative of (I) similarly gives chloroacetyldulcine (N' -chloroacetyl- N - p -phenethylcarbamide) (III), m.p. 181–182° [also obtained as a by-product with (II), or directly from (I)], or, with BzCl, benzoyldulcine (N' -benzoyl- N - p -phenethylcarbamide) (IV), m.p. 215–217° [also obtained from (I) and BzCl in C_5H_5N]. Similarly the (MgBr)₂ derivative yields dibenzoyldulcine (NN'-dibenzoyl- N - p -phenetyl-

carbamide), m.p. 170—171°, slowly hydrolysed only by 30% EtOH-KOH or 20% HCl; ($\text{CH}_2\text{-NHBz}$)₂ is similarly resistant. The new compounds are tasteless.

VI. At 215—220° (bath), (III) gives ($\text{p-OEt-C}_6\text{H}_4\text{-NH}$)₂CO (V), $\text{CH}_2\text{Cl-CN}$, $\text{CH}_2\text{Cl-CO-NH}_2$, and CO_2 ; at 260—270° (bath), (IV) gives (V), PhCN, NH_2Bz , NH_3 , and CO_2 . E. W. W.

Decomposition of diazo-perbromides derived from azobenzene. P. P. HOFF and R. J. W. LE FÈVRE (J.C.S., 1939, 1067—1068).—Azobenzene-4-diazoperbromide (I), m.p. ~62° (decomp.), refluxed in AcOH or EtOH affords 4:4'-dibromo- or 4-bromoazobenzene (II) respectively; (I) at ~60° gives (II). 2:4-Diaminoazobenzene with NaNO_2 -aq. H_2SO_4 and then Br-HBr gives a diperbromide, m.p. ~109° (decomp.), converted by heat into an insol. substance, m.p. >290°, also formed, together with (?) 2:4:4'-tribromo- or 2:4-dibromoazobenzene, by decomp. in boiling AcOH or EtOH, respectively. A. T. P.

(A) Action of benzenediazonium chloride on α -substituted γ -butyrolactones. (B) Interaction of α -cyano- γ -butyrolactone with benzenediazonium chloride. V. V. FEFILAKTOV and A. S. ONISCHTSCHENKO (J. Gen. Chem. Russ., 1939, 9, 314—324, 325—330).—(A) α -Aceto- γ -butyrolactone or γ -butyrolactone- α -carboxylic acid and aq. PhN_2Cl at 0° yield the phenylhydrazone (I) of α -keto- γ -butyrolactone, whilst with Et γ -butyrolactone- α -carboxylate the product is α -benzenazo- α -carbethoxy- γ -butyrolactone, an oil, hydrolysed by aq. NaOH to the phenylhydrazone of γ -hydroxy- α -ketobutyric acid. (I) is reduced to α -amino- γ -hydroxybutyric acid by Sn in aq. HCl, and to the phenylhydrazone of 2-hydroxy-3-ketotetrahydrofuran, m.p. 104—105°, by Al-Hg in H_2O .

(B) α -Cyano- γ -butyrolactone and PhN_2Cl at 0—3° yield α -benzenazo- α -cyano- γ -butyrolactone, m.p. 101—102° (decomp.), which with NaOH in EtOH at room temp. gives the phenylhydrazone of γ -hydroxy- α -ketobutyronitrile (II), m.p. 168—170°, the hydrochloride, m.p. 147—148° (decomp.), of which yields (I) with boiling H_2O . (II) and H_2O at the b.p. give the phenylhydrazone of γ -hydroxy- α -ketobutyramide, m.p. 162—163°, converted into (I) by heating with dil. aq. HCl. R. T.

Oxidation of lithium phenyl. H. A. PACEVITZ and H. GILMAN (J. Amer. Chem. Soc., 1939, 61, 1603—1604).—Air converts LiPh in C_6H_6 (prep. in N_2) into PhOH (22—25.9%), Ph_2 (22.6—25%), and small amounts of $\text{p-C}_6\text{H}_4\text{Ph-OH}$ (possibly derived by metalation of Ph_2). Ph_2 is also formed when LiPh inflames in air. Solid LiPh, NaPh, and KPh are chemiluminescent when oxidised. R. S. C.

System acetamide-phenol. S. D. BOON (Rec. trav. chim., 1939, 58, 600—602).—The findings of Kremann and Wenzing (A., 1918, i, 218) are incorrect, probably owing to the use of impure NH_2Ac . In addition to 2PhOH, NH_2Ac , there is also a compound, $\text{PhOH-NH}_2\text{Ac}$, which undergoes decomp. (below the m.p.) at ~34°. There are two eutectics, at 27.5° and 32.5°. F. J. G.

Production of nitrosophenols.—See B., 1939, 697.

Alkyl-cresols and -naphthols.—See B., 1939, 777.

Orientation of 3:4-benzpyrene in substitution reactions. L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1939, 61, 1565—1574).—Detailed arguments, based on the following results and those described earlier (Fieser *et al.*, A., 1938, II, 273, 486) and by Windaus *et al.* (A., 1937, II, 491; 1939, II, 106), show that 3:4-benzpyrene (I) is attacked exclusively at C_{15} by Pb(OAc)_4 , NPhMe-CHO , diazonium salts, Cl_2 , and on nitration. With AcCl and SnCl_4 in PhNO_2 , (I) gives 72% of a ketone mixture, whence are obtained 26% of 10-acetyl-3:4-benzpyrene (II), m.p. 190—190.5°, and a little (? 8-)acetyl-3:4-benzpyreneoxime, m.p. 220—223° [Beckmann rearrangement gives (? 8-)acetamido-3:4-benzpyrene, m.p. 269—270°]. The structures of the H_x -derivatives marked * below are confirmed by or based on absorption max. and general shape of the absorption curves. Diazotisation of 5-amino-3:4-benzpyrene proceeds abnormally; the 5-OH-derivative could not be obtained therefrom, probably because of its sensitivity. 3:4-Benzpyrene-5-aldehyde (III) resists oxidation; its oxime, m.p. 241—243° (decomp.), and $\text{Ac}_2\text{O-AcOH}$ give the 5-nitrile, m.p. 237.4—237.7°, which does not react with MgMeCl or MgMeBr . With MgMeCl , (III) gives 5- α -hydroxyethyl-3:4-benzpyrene, m.p. 141—141.5°, largely unchanged by NaOI. With H_2 -Raney Ni in EtOH, (II) gives 10- α -hydroxyethyl-3:4-benzpyrene, m.p. 146—153°, but, after resolidification, 153—154°; $\text{Al(OPr}^t)_3$ in hot C_6H_6 is ineffective. 3:4-Trimethylenebenzanthrone-7 with S gives tars; with Zn dust and NaOAc in Ac_2O it gives 5-acetoxy-6:8:9:10-tetrahydro-3:4-benzpyrene, m.p. 168.5—169°, which could not be methylated, with PdO at 300° gives 70% of benzpyrene (IV), and with Pt (Adams)-Pd- H_2 in EtOAc-AcOH gives 5-acetoxy-6:7:7a:8:9:10-hexahydro-3:4-benzpyrene (V), m.p. 182.8—183.3°. KOH-MeOH hydrolyses (V) to the phenolic 5-OH-compound*, m.p. 163—164°, which in coupling tests gives diazo-ethers. MgBu^tBr , followed by Me_2SO_4 , converts (V) into 5-methoxy-6:7:7a:8:9:10-hexahydro-3:4-benzpyrene, m.p. 135.5—136.5°, which with S in quinoline gives indefinite products and with Pd-C at 270—275° gives a little (IV) only. Further hydrogenation (Pt-Pd- FeCl_2 , AcOH) of (V) yields (?) 5-acetoxy-3:4-tetramethylene-3:4:5:8:9:10-hexahdropyrene, m.p. 124—126°, hydrolysed by KOH-MeOH to the 5-OH-compound*, m.p. 167—168°. 5-Acetoxy-3:4-benzpyrene (VI) with MgBu^tBr gives 5-hydroxy-3:4-benzpyrene (VII), m.p. 207—209° (decomp.; bath preheated at 205°), sol., but unstable, in aq. alkali (does not couple with $\text{p-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$). With MgBu^tBr , followed by Me_2SO_4 , (VI) gives 5-methoxy-3:4-benzpyrene, m.p. 174—174.5°, with H_2 -Pt-Pd in AcOH-EtOAc gives 5-acetoxy-3:4-tetramethylenepyrene, m.p. 182—183° [with PdO in AcOH at 300° gives (IV)]; hydrolysed by KOH-MeOH to the phenolic 5-OH-compound*, m.p. 181.5—182°, which yields diazo-ethers in coupling tests], and with H_2 -Pt-Pd in AcOH gives 5-acetoxy-3:4-tetramethylene-6:7- or -1:2-dihdropyrene, m.p.

135.5—136° (hydrolysed to the 5-OH-compound*, m.p. 139.5—140°, which gives diazo-ethers). 5-Amino-3:4-benzpyrene (VIII), m.p. 237—239° (decomp.), is obtained from the 5-NO₂-compound (prep. modified to give a 73% yield), m.p. 254—255°, by H₂-PtO₂ in EtOAc (91% yield; cf. Windaus, *loc. cit.*) and from 5-*p*-nitrobenzenazo-3:4-benzpyrene by SnCl₂-HCl. With HNO₂ in AcOH-H₂SO₄, (VIII) gives 3:4-benzpyrene-5:10-quinone and thence 5:10-diacetoxy-3:4-benzpyrene (IX), obtained similarly from (VII). When Ac₂O and NaOAc are added to (VIII) in EtOAc-AcOH, 89% of the N-Ac₁ derivative, m.p. 345—350° (decomp.; block), is obtained; with Pb(OAc)₄ in AcOH this gives 5-acetamido-(? 10)-acetoxy-3:4-benzpyrene, m.p. 245—255° (decomp.), hydrolysis of which gives indefinite results. With boiling Ac₂O, (VIII) gives the Ac₂ derivative, m.p. 224.5—225.5° (Windaus, *loc. cit.*, 217.5°). With *iso*-C₅H₁₁·O·NO in AcOH-H₂SO₄ or HNO₃ (*d* 1.5) in AcOH at 40°, (VI) gives 10-nitro-5-acetoxy-3:4-benzpyrene, m.p. 259.5—260° (decomp.), which with H₂-PtO₂ in EtOAc gives 10-amino-5-acetoxy-3:4-benzpyrene (X), m.p. 221—222°; when hydrolysed by dil. H₂SO₄, this gives by oxidation the 5:10-quinone, identified as (IX). 10-Acetyl-3:4-benzpyreneoxime, m.p. 264—267°, yields 10-acetamido-3:4-benzpyrene, m.p. 334—337° (decomp.; block), oxidised by Pb(OAc)₄ in AcOH to 10-acetamido-5-acetoxy-3:4-benzpyrene, m.p. 325—330° (decomp.; block), obtained also from (X) by Ac₂O; this completes the proof of the structure of (II) and the derived compounds. M.p. (<300°) are corr.

R. S. C.

α - and β -Leprosol. A. BUTENANDT and F. H. STODOLA (Annalen, 1939, 539, 40—56).—Diagnostic colour reactions and absorption spectra of mono-, di-, and tri-alkylresorcinols indicate that normethyl- α - and - β -leprosol (A) [obtained (A., 1936, 1028, where they are termed "substances") from α - and β -leprosol by HI] are 4:5:6-trialkylresorcinols. (A) give the deep blue colour with NH₃ and phosphomolybdate and the white ppt. with Hg(NO₃)₂ characteristic of *m*-C₆H₄(OH)₂ derivatives, but do not give the reactions characteristic of *o*- and *p*-C₆H₄(OH)₂ derivatives; however, they do not give the fluorescein or Guareschi (CHCl₃-alkali) test. Normethyl- β -leprosol (I) in Et₂O has a sharp absorption max. at 287 m μ . 2-*iso*-Amyl-, 4-*octadecyl*-, (II), and 5-*tetradecyl*-resorcinol (III) give the Guareschi test; absorption max. of (II) and (III) in Et₂O are at 283 and 277 m μ ., respectively. (A) are not 2:5-dialkylresorcinols, since such symmetry does not account for the varying ease of methylation of the 2 OH of (I). 2:4- and 4:5-Di- and 2:4:5-tri-alkylresorcinols, having a free position *p*- to the OH, would probably give Guareschi and Liebermann reactions. 4:6-Diethyl- and 4-ethyl-6-*octadecyl*-resorcinol (IV) also give a fluorescein reaction; their absorption max. are at 287 m μ ., but ϵ is 20% > that of (I). 2:4:6-Trialkylresorcinols probably give a fluorescein reaction. 4:5:6-Trimethylresorcinol (V) closely resembles (A) in colour reactions and its absorption max. is at 287 m μ ., ϵ being only 10% > that of (I). Coupling of bromo- α -leprosol with *p*-NO₂-C₆H₄-N₂Cl (*loc. cit.*) must be accompanied by loss of a substituent. *m*-C₆H₄(OH)₂, stearic acid

(VI), and anhyd. ZnCl₂ at 135—150° give 4-stearoyl-resorcinol, reduced by Zn-Hg-HCl to (II), m.p. 92—93°. 3:5-(OH)₂C₆H₃-CO₂H and Me₂SO₄-NaOH give the Me₂ ether, m.p. 181—182°, converted by H₂SO₄-MeOH into its Me ester, m.p. 43—44°, which yields Et 3:5-dimethoxybenzoylacetate. With *n*-C₁₂H₂₅I and NaOEt in dry EtOH this gives 3:5-(OMe)₂C₆H₃-CO-CH(C₁₂H₂₅-*n*)-CO₂Et, hydrolysed by boiling H₂SO₄-H₂O-AcOH (1:1:20) to 5-myristoylresorcinol Me₂ ether, m.p. 60—61°, which is reduced (Clemmensen) and then demethylated (HI) in poor yield to (III), m.p. 89.5—90.5°. 4:1:3-C₆H₃Et(OH)₂, (VI), and anhyd. ZnCl₂ at 140—150° give 20% of 6-stearoyl-4-ethylresorcinol, m.p. 89—90°, and thence (Clemmensen) (IV), m.p. 70.5—72° and then 77—78°. 2:4:6:1-(OH)₂C₆H₂Me·CHO [prep. from 5:1:3-C₆H₃Me(OH)₂ by Zn(CN)₂ and HCl], m.p. 180—181° (lit. 178—180°), and Zn-Hg-HCl give 4:5-dimethylresorcinol, m.p. 135—136°, which with Zn(CN)₂ and HCl gives 2:4-dihydroxy-5:6-dimethylbenzaldehyde (64% yield), m.p. 196—197°, and thence (Clemmensen) (V), m.p. 162.5—163.5° (lit. 163—164°).

R. S. C.

Preparation of *p*-nitrophenetole from *p*-chloronitrobenzene.—See B., 1939, 694.

Reactions with boron fluoride. XXII. Methylation of aromatic compounds by methyl ether-boron fluoride. A. J. KOLKA and R. R. VOGT (J. Amer. Chem. Soc., 1939, 61, 1463—1465).—Boiling Me₂O·BF₃ converts PhOH or PhOMe into PhOMe (from PhOH), mono-, di-, tri-, tetra-, and penta-methylanisole (I) (with Ac₂O-50% HI at 135° followed by hydrolysis gives C₆Me₅·OH), the yields of which depend on the relative wts. of the reactants and the time of heating. Nitration of a fraction containing probably C₆HMe₄·OMe gave a compound, m.p. 189°.

R. S. C.

Labile union of oxygen to carbon; a peroxide which dissociates spontaneously in the cold. C. DUFRAISSE, L. VELLUZ, and (MME.) L. VELLUZ (Compt. rend., 1939, 208, 1822—1824).—1:4-Dimethoxy-9:10-diphenylanthracene (I) gives a colourless cryst. photo-9:10-dioxide (II) when irradiated in solution in air. Decomp. of (II), giving (I) and O₂, occurs slowly at 20° (25 and 78% respectively in 10 and 40 days), and completely at 80° in <1 hr. (II) is thus unusually unstable.

A. J. E. W.

Manufacture of *o*- and *p*-nitrophenyl trifluoromethyl sulphones and intermediate products.—See B., 1939, 696.

Reduction of 2-bromocyclohexanone with aluminium isopropoxide. S. WINSTEIN (J. Amer. Chem. Soc., 1939, 61, 1610).—2-Bromocyclohexanone and Al(OPrⁱ)₃-PrⁱOH give 30% of 2-bromocyclohexanol and 33% of cyclohexanol, but no unsaturated compounds (cf. Stevens, A., 1939, II, 61).

R. S. C.

Determination of the configuration of 1:3-substituted cyclohexanols. A. SKITA and W. FAUST (Ber., 1939, 72, [B], 1127—1138).—*m*-5-Xylenol (I) is hydrogenated (230°/50 atm., Ni-kieselguhr) to a little 1:3-dimethylcyclohexane and a mixture of carbinols which is oxidised and separated through

the oximes into 3°:5^t-dimethylcyclohexanone (II), b.p. 64°/15 mm. (semicarbazone, m.p. 193—194°), and 3°:5^c-dimethylcyclohexanone (III), b.p. 66.5°/18 mm. (semicarbazone, m.p. 202—203°). Reduction of (II) by Na in moist Et₂O or catalytically (colloidal Pt in AcOH) affords 3°:5^t-dimethylcyclohexan-1^c-ol, b.p. 84°/17 mm. (3:5-dinitrobenzoate, m.p. 66.5—67°), accompanied in the case of alkaline reduction by 1:1'-dihydroxy-3°:5^t:3°:5^t-tetramethyldodecahydrodiphenyl, m.p. 140—141°. Catalytic reduction (colloidal Pt in AcOH) of (III) and similar treatment or pressure hydrogenation (Ni-kieselguhr in Et₂O at 180°) of (I) yields 3°:5^c-dimethylcyclohexan-1^c-ol, b.p. 79—80°/17 mm., m.p. 39—40° (3:5-dinitrobenzoate, m.p. 133—134°), with in the second instance 1:3-dimethylcyclohexane, b.p. 118.5—119.5°/750 mm. Reduction (Na in moist Et₂O) of (III) or hydrogenation (colloidal Pt in EtOH without addition of acid) of (I) affords 3°:5^c-dimethylcyclohexan-1^c-ol, b.p. 84—85°/18 mm., m.p. 16° (3:5-dinitrobenzoate, m.p. 77—78°), and, in the case of alkaline reduction, a product, C₁₆H₃₀O₂, m.p. 140—141°. The 3:5-dimethylcyclohexanols do not conform to von Auwers' rule according to which the *cis*-compounds have higher vals. of *d* and *n* than the *trans*-substances. H. W.

Alkanolamines. VI. Physiologically active compounds. I. Preparation of substituted anilino-alcohols. C. B. KREMER (J. Amer. Chem. Soc., 1939, 61, 1321—1324).—Prep. of *N*-γ-bromo-*n*-propyl-, m.p. 72—73°, and ε-bromo-*n*-amyl-phthalimide (75% yield), cryst., and thence by hot 20% KOH of OH·[CH₂]₃·NH₂ (85%), b.p. 185—186°, and OH·[CH₂]₅·NH₂ (60%), b.p. 270—271°, is described. C₆H₄Cl·NO₂ and the appropriate OH-amine with or without anhyd. Na₂CO₃ give *o*- (60%), m.p. 76—76.5°, and *p*-nitro-*N*-β-hydroxyethylaniline (20%), m.p. 110—110.5°, *o*- (80%), m.p. 60.5—61°, and *p*-nitro-*N*-γ-hydroxy-*n*-propylaniline (80%), m.p. 74—74.5°, *o*- (55%), m.p. 67.5—68.5°, and *p*-nitro-*N*-β-hydroxy-*n*-propylaniline (20%), m.p. 85.5—86°, *o*- (I) (90%), m.p. 80—80.5°, and *p*-nitro-*N*-β-hydroxyisobutylaniline (85%), m.p. 114—114.5°, and *o*-nitro-*N*-ε-hydroxy-*n*-amylaniline (90%), b.p. 200—201°/1 mm.; some C₆H₄Cl·NH₂ and azo-compound accompanied with the Et and Pr derivatives. Sn-HCl or Na₂S₂O₄-KOH then yields *o*-, m.p. 106—106.5° (hydrochloride, m.p. 144.5—145.5°), and *p*-amino-*N*-β-hydroxyethylaniline, unstable [hydrochloride, m.p. 198—199° (decomp.)], *o*-amino-*N*-γ-hydroxy-*n*-, m.p. 65.5—66° (hydrochloride, m.p. 146.5—147°), and *o*-amino-*N*-β-hydroxy-*n*-propylaniline, m.p. 85.5—86.5°, and *p*-amino-*N*-β-hydroxyisobutylaniline, m.p. 107.5—108°. With HCl in Et₂O the bases give first unstable dihydrochlorides. With Sn-HCl, (I) gives a substance, m.p. 98—99°, which is not the expected OH-diamine. M.p. are corr. R. S. C.

Reaction of adrenaline with mercuric salts.—See B., 1939, 775.

Action of Grignard reagents on oximes. I. Action of magnesium phenyl bromide on mixed ketoximes. K. N. CAMPBELL and J. F. McKENNA (J. Org. Chem., 1939, 4, 198—205).—The “α-hydroxylamino-α-diphenylpropane” of Hoch (A., 1934, 893) is β-amino-α-diphenylpropan-α-ol (I), m.p. 103—

104°, which is obtained from CPhEt·N·OH [at 155—165° (bath)] or CO₂Et·CHMe·NH₂·HCl and MgPhBr. *p*-C₆H₄Me·CMe·N·OH and α-C₁₀H₇·CMe·N·OH with MgPhBr similarly give β-amino-α-phenyl-α-*p*-tolyl- and -α-phenyl-α-1-naphthyl-ethyl alcohol, respectively, also synthesised from CPh·CH₂·NH₂·HCl and *p*-C₆H₄Me·MgBr or 1-C₁₀H₇·MgBr, respectively. *p*-C₆H₄Cl·CMe·N·OH or *p*-C₆H₄Cl·CO·CH₂·NH₂·HCl and MgPhBr give β-amino-α-phenyl-α-*p*-chlorophenyl-ethyl alcohol, m.p. 121.5—122° (hydrochloride, m.p. 203°; nitrate, m.p. 183°; *N*-Bz derivative, m.p. 147—148°). A. T. P.

Therapeutically active triphenylmethane dyes. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1939, 4, 58—68).—Conc. H₂SO₄ is added to fused 2:1 guaiacol-vanillin mixture, and the mass kept for 5—7 days at room temp., when tri-(4-hydroxy-3-methoxyphenyl)-methane, m.p. 88—90°, is obtained. This is oxidised (amyl nitrite and HCl) to tri-(4-hydroxy-3-methoxyphenyl)carbinol (compound with NaHSO₃). Analogous compounds (not described) are obtained from guaiacol- or guetol-bourbonal and guetol-vanillin mixtures. R. T.

Colour reaction of Tortelli and Jaffé. U. WESTPHAL (Ber., 1939, 72, [B], 1243—1246).—Among steroids the colour reaction is usually positive only if the compound has a *ditert.* double linking within the ring system. Such double linkings in the side-chain or in the semicyclic position are not causative of colour. The position of ergosterol (I) and dehydroergosterol is exceptional probably by reason of the ready displaceability of the double linkings of the ergosterol system. Δ^{5:7}-Androstadiene-3:17-diol, which has the same system of double linkings in ring B as (I), gives only a faint reaction. The acetates give the same reactions as the corresponding free alcohols but colour is not observed with the benzoates. H. W.

α- and β-Cholestyl chlorides. T. KAWASAKI (J. Pharm. Soc. Japan, 1938, 58, 53—56).—α-Cholestyl chloride (I) is unaffected by EtOH-NaOEt or -KOH but the more reactive, less stable β-cholestyl chloride (II), m.p. 105—106°, gives neocholestene. KOAc and AgOAc in C₅H₅N are without action on (I) but (II) and AgOAc (not KOAc) in C₅H₅N at 100° (bath)/5 hr. afford cholestanyl acetate. The total Cl of (II) is eliminated by boiling BuOH-NaOH during 2—3 hr.; (I) is similarly little affected and it is thus possible to determine (II) in admixture with (I) (or cholesteryl chloride). (II) is readily obtained pure from cholestanol and PCl₅ in CHCl₃; a smaller amount of cryst. material, m.p. 92—99°, is isolable from the mother-liquors and this gives (II) when freed from unsaturated matter by Anderson's method (A., 1924, i, 1217). The 2:3-dibromocholestanes (neocholestene dibromides, m.p. 122° (III) and 144° (IV), from their behaviour with NaOBu, are now correctly designated β-[=(II)] and α-[=(I)], respectively; (III) heated to 200° undergoes quant. conversion into (IV). When (II) is heated to 240—250° (no change at 200°), some HCl is eliminated, a substance, m.p. ~77°, is formed, and partial conversion into (I) appears to occur. Cholestanol Me ether and

(I) form mixed crystals; with (II) a 1:1 eutectic is apparently produced.

H. B.

α - and β -Cholestyl bromides. T. KAWASAKI (J. Pharm. Soc. Japan, 1938, 58, 157—159).—Cholestanol (I) and PBr_3 in boiling C_6H_6 give β -cholestyl bromide (II), m.p. 103—104° when purified by Anderson's method (A., 1924, i, 1217). Wagner-Jauregg's bromide (cf. A., 1933, 271) is probably a mixture of (II) and the α -bromide (III). Necholestene is obtained from (II) by boiling BuOH-NaOBu or by chromatography (Al_2O_3); (III) is more stable. (II) and (III) are probably *trans*- and *cis*-bromides, respectively. Cholestanol Me ether forms a eutectic with (II) and mixed crystals with (III). Dicholestanyl phosphite, $(\text{C}_{27}\text{H}_{47}\text{O})_2\text{P}\cdot\text{OH}$, m.p. 186°, is obtained from (I) and PBr_3 in cold C_6H_6 .

H. B.

*iso*Dehydroergosterol as a component of *iso*-neorgosterol, a molecular compound obtained from the pyrolysis of ergopinacone. T. ANDO (Bull. Chem. Soc. Japan, 1939, 14, 169—172).—Hydrolysis (1% EtOH-KOH) of the 3:5-dinitrobenzoate, m.p. 187.5—189.5°, from *isoneoergosterol* (I) yields "*isodehydroergosterol*," $\text{C}_{28}\text{H}_{42}\text{O}$ (?), m.p. 128—129.5° (corr.), $[\alpha]_D^{20}$ —102° in CHCl_3 , which is pptd. by digitonin, and differs from dehydroergosterol. A mixture of this with neorgosterol when cryst. from COMe_2 yields (I), a mol. compound of the two.

A. LI.

Hydrogenation of *isoergosterone*. B. GÜNTZEL (Ber., 1939, 72, [B], 1317—1318).—*isoErgosterone* is converted by $\text{Al}(\text{OPr}^i)_3$ in Pr^iOH into $\Delta^{4:6:22}$ -*ergostatrien-3-ol*, m.p. (hydrate) 125—128°, $[\alpha]_D^{20}$ —96.2° in CHCl_3 (acetate, m.p. 106°, $[\alpha]_D^{20}$ —118.8° in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 124°), which gives a digitonide (I). The mother-liquors from (I) contain an *epi*-derivative.

H. W.

Constitution of cafesterol. I. H. HAUPTMANN and J. FRANÇA (Z. physiol. Chem., 1939, 259, 245—250; cf. Slotta *et al.*, A., 1939, II, 18).—Dehydrogenation (Se) of cafesterol (I), $\text{C}_{20}\text{H}_{28}\text{O}_3$, yields an oily hydrocarbon, $\text{C}_{18}\text{H}_{16}$, with the characteristic fluorescence. The side-chain on C_{17} probably has only one C. The OH which is easily acetylated is primary and adjacent to a *tert*.-OH. Anhydrocafersterol (*loc. cit.*) contains CHO. Ring A is probably not aromatic and Me is probably present at C_{10} . Hydrogenation (PtO_2) of the acetate (II) yields a H_6 -derivative (III), but if only small amounts of PtO_2 are used, the third H_2 is absorbed only slowly. Titration of (II) with permanganic acid indicates 2 double linkings and excludes presence of a C_6H_6 ring. The third O is present either as an oxide ring or preferably as a difficultly reactive CO, since (III) contains 2, whilst (I) and (II) contain 2 and 1, active H, respectively. A possible structure is suggested.

J. N. A.

Reaction of cholesterol α -oxide with magnesium methyl iodide. M. I. USCHAKOV and O. S. MADAEVA (J. Gen. Chem. Russ., 1939, 9, 436—441).—Cholesterol α -oxide (I) does not react with LiMe or MgMe_2 at 80—100°. With MgMeI in boiling $\text{Et}_2\text{O-C}_6\text{H}_6$ it yields 6-methylcholestan-3:5-diol (I), m.p. 181—181.5° (corr.), which with Ac_2O gives the 3-acetate, m.p. 164—165°, from which 6-methylchol-

Z (A., II.)

esteryl acetate, m.p. 115—115.5°, is obtained by adding conc. H_2SO_4 ; this is hydrolysed (KOH-EtOH) to 6-methylcholesterol, m.p. 134.5—135°. (I) and CrO_3 in AcOH at 36° give 6-methylcholestan-5-ol-3-one, m.p. 211—212°, converted by HCl in CHCl_3 into 6-methyl- Δ^4 -cholesten-3-one, m.p. 126.5—127.5°.

R. T.

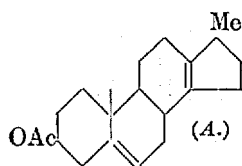
Steroids and related compounds. III. Constitution of Westphalen's diol. V. A. PETROW (J.C.S., 1939, 998—1003; cf. A., 1938, II, 277).—Further evidence in support of the formulation of Westphalen's diol as 5-methyl- $\Delta^{8:9}$ -norcholestene-3:6-diol is obtained. 5-Hydroxy-3:6-diacetoxycholestan-3-one, KHSO_4 , and Ac_2O (best) or $(\text{EtCO})_2\text{O}$ at 100° (bath) give improved yields of Westphalen's diacetate (I) (A., 1915, i, 884), which with Se at 300—310° (1 hr.), then at 340—360° (40 hr.), gives the " $\text{C}_{25}\text{H}_{24}$ " hydrocarbon, m.p. 224—225°, a typical dehydrogenation product of cholesterol containing the cyclopentenophenanthrene ring (cf. Diels *et al.*, A., 1934, 288). 5-Methyl- $\Delta^{8:9}$ -norcholestene-3:6-dione and H_2O_2 - AcOH at room temp. give 5-methylnorcholestan-3:6-dione 8:9-oxide (II), m.p. 132—133° (softens at 120°), $[\alpha]_D^{20}$ —35° (all rotations in CHCl_3) [mono-*o*-tolylsemicarbazone, m.p. 224—225° (decomp.)]. (I) and $\text{BzO}_2\text{H-CHCl}_3$ or H_2O_2 - AcOH at room temp. give 3:6-diacetoxy-5-methylnorcholestan-8:9-oxide (III), m.p. 132.5—133.5°, $[\alpha]_D^{20}$ +8.7° [unaffected by 2:4-(NO_2) $_2\text{C}_6\text{H}_3\text{-NH-NH}_2$ or $\text{Ac}_2\text{O-NaOAc}$], hydrolysed by KOH-EtOH to 5-methylnorcholestan-3:6-diol 8:9-oxide, m.p. 174.5—175.5°, $[\alpha]_D^{20}$ +35.5°, which is oxidised by CrO_3 - AcOH at room temp. to (II). Westphalen's diol and SeO_2 - EtOH at room temp. give 5-methyl- $\Delta^{8:9}$ -norcholestene-3:6:11-triol, m.p. 223° (decomp.), which with $\text{Ac}_2\text{O-C}_6\text{H}_5\text{N}$ affords the 3:6-diacetate (IV), m.p. 183.5—184.5°, $[\alpha]_D^{20}$ —21°. The inert character of the OH at C_{11} is shown by its resistance to acylation and to oxidation (Oppenauer). (IV) is oxidised (CrO_3) at room temp. to 3:6-diacetoxy-5-methylnorcholestan-11-one 8:9-oxide (V), m.p. 159.5—160.5°, $[\alpha]_D^{20}$ +121° [does not react with Ac_2O , NH_2OH , or 2:4-(NO_2) $_2\text{C}_6\text{H}_3\text{-NH-NH}_2$], also obtained from (I) and CrO_3 -aq. AcOH at 55—60° [through (IV)]. (V) and KOH-MeOH afford 5-methylnorcholestan-3:6-diol-11-one 8:9-oxide, m.p. 219—220° (sinters at 203°), $[\alpha]_D^{20}$ +123°, oxidised by CrO_3 - $\text{AcOH-C}_6\text{H}_6$ to 5-methylnorcholestan-3:6:11-trione 8:9-oxide, m.p. 165.5—166.5°, $[\alpha]_D^{20}$ +134°, which does not react with $\text{Pb}(\text{OAc})_2$, *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, $\text{Ac}_2\text{O-NaOAc}$, HCl-CHCl_3 , or $\text{EtOH-H}_2\text{SO}_4$. (III) and HCl-EtOH , then $\text{Ac}_2\text{O-NaOAc}$, or (IV) and $\text{Ac}_2\text{O-NaOAc}$, give α :3:6-diacetoxy-5-methyl- $\Delta^{8-14:9-11}$ -norcholestadiene (VI), m.p. 126—127°, $[\alpha]_D^{20}$ —45.8°, and a β -isomeride (VII), m.p. 167.5°, $[\alpha]_D^{20}$ —36.6° (absorption spectra examined), hydrolysed by KOH-EtOH to the corresponding 5-methyl- $\Delta^{8-14:9-11}$ -norcholestadiene-3:6-diol, α -, m.p. 95—102°, $[\alpha]_D^{20}$ —46.7° (typical 3-banded spectrum of high intensity resembling that of ergosterol, indicating a system of conjugated linkings in one ring), and β -form (probably $\Delta^{1-10:9-11}$), m.p. 182°, $[\alpha]_D^{20}$ —47° (single band of low intensity indicates a system of conjugated ethylenic linkings spread over 3 rings). Maleic anhydride and (VII) give an adduct [corresponding acid, m.p. 190° (decomp.)] in C_6H_6 at 80°.

whereas (VI) forms an adduct (corresponding acid, m.p. 213°) only at 135° (in xylene). Catalytic hydrogenation (Pd-C; Et₂O-AcOH) of (VI) or (VII) affords a poor yield of (I); (VI) is unchanged by Na + EtOH but (VII) gives (after acetylation) some (I).

A. T. P.

Sterols. LXIV. 2:3-Dihydroxyandrostane derivatives. R. E. MARKER and L. PLAMBECK, jun. (J. Amer. Chem. Soc., 1939, 61, 1332—1333).—Δ²-Cholestene and H₂O₂ in AcOH at 100° give 2:3-dihydroxycholestane, m.p. 195—197° (201° when regenerated from the diacetate, m.p. 133—135°), the structure of which is shown by oxidation by CrO₃-AcOH at 60° to the acid, C₂₅H₄₄(CO₂H)₂, m.p. 193°, obtained also from cholestanol. Androsten-17-one and H₂O₂ give 2-hydroxyandrostosterone (difficult to purify), m.p. 195—198°, reduced (Na-Pr^oOH) to 2:3:17-trihydroxyandrostane, m.p. 264° (triacetate, m.p. 188°), which is also obtained from androsten-17-ol by H₂O₂. The 3-OH of the products may have the *epi*-configuration, as digitonides are not obtained. R. S. C.

17-Chloro-derivatives of the testicular hormone and their transformation products. U. WESTPHAL, Y. L. WANG, and H. HELLMANN (Ber., 1939, 72, [B], 1233—1242).—The desired 17-Cl-derivatives are readily obtained but elimination of HCl is accompanied by isomerisation so that the products are unsuitable materials for the prep. of 16:17-glycols. Dehydroandrosterone acetate is converted by catalytic hydrogenation (Raney Ni in EtOH) or by help of fermenting yeast into Δ⁵-androsterone-3:17-diol 3-monoacetate, m.p. 144—145°, [α]_D²⁰ -55.8° in EtOH, which is transformed by PCl₅ in CHCl₃ containing CaCO₃ into 17-chloro-Δ⁵-androsterone-3-ol 3-acetate, m.p. 160—161°, [α]_D²⁰ -56.5° in CHCl₃. This is converted by KCN and KI in MeOH or



85% EtOH at 120° into retro-androstadien-3-ol 3-acetate (A), m.p. 75°, [α]_D²⁰ +68.0° in EtOH, which gives a yellow colour with C(NO₂)₄ in AcOH and is converted by successive treatments with OsO₄ in Et₂O and Na₂SO₃ in H₂O-EtOH into the retro-androstene-3:13:14-triols, cubes, m.p. 223° after softening at 218°, and needles, m.p. 152—153°. The former with Ac₂O in abs. C₅H₅N at room temp. gives the 3-monoacetate, m.p. 144—146°, which is not further acetylated by Ac₂O-C₅H₅N at 100°. Dehydroandrosterone acetate appears to be largely unchanged by OsO₄ in Et₂O at room temp. Testosterone is transformed by PCl₅ in CHCl₃ containing CaCO₃ into testosterone phosphate (+1H₂O), m.p. 160° (decomp.), 17-chloro-Δ⁴-androsten-3-one, m.p. 148°, and 3:17-dichloro-Δ^{3:5}-androstadiene, m.p. 127°. Estradiol monobenzoate, m.p. 194—195°, affords 17-chloro-estratrien-3-ol 3-benzoate (I), needles or prisms, m.p. 158°, [α]_D²⁵ +16.6° in CHCl₃, and a compound, C₂₅H₂₇O₂Cl.C₂₅H₂₆O₂, m.p. 123°; in an individual experiment an isomeric chloro-estratrien-3-ol 3-benzoate, m.p. 198° (slight decomp.), was isolated. Removal of HCl from (I) by KCN-KI in aq. EtOH at 120—125° gives retro-estratetraen-3-ol, (II), m.p. 163°, [α]_D²⁵ -35.0° in abs. CHCl₃, whereas NaOAc and KI in 80% EtOH at 125° give retro-

estratetraen-3-ol 3-benzoate (III), m.p. 159°, [α]_D²⁵ +17.8° in abs. CHCl₃, hydrolysed to (II). The mother-liquors from (III) contain an isomeric benzoate, m.p. 133°, [α]_D²⁵ +69.3° in abs. CHCl₃, hydrolysed to a compound, m.p. 125°. (II) is transformed by OsO₄ in Et₂O followed by Na₂SO₃ into retro-estratriene-3:13:14-triol, m.p. 241°, whereas an impure tetraenol when similarly treated yielded a triol, C₁₈H₂₄O₃.0.5H₂O, m.p. 187°.

H. W.

Thiocyano-derivatives of hydnocarpic and chaulmoogric acids. H. ARNOLD (Arch. Pharm., 1939, 277, 206—211).—Hydnocarpic acid and (CNS)₂ (prepared *in situ*) in AcOH give 2:3-dithiocyanodihydrohydnocarpic acid. Impure Et 2:3-dithiocyanodihydrochaulmoogric acid is similarly prepared. 3-Thiocyanodihydrochaulmoogric acid (Et ester, b.p. 200—230°/0.3 mm.) is obtained from the 3-Br-acid by NaCNS in AcOH. None of these products (all oils) cures leprosy in mice.

R. S. C.

Synthesis of alkoxyphenylacetic acids. G. HAHN and H. J. SCHULZ (Ber., 1939, 72, [B], 1302—1308).—α-Chloroalkoxyphenylacetamides (I) (occasionally hydrolysed by warm H₂O to the corresponding mandelamides) are hydrolysed to the mandelic acids, which are reduced by Pd in AcOH to the alkoxyphenylacetic acids or, preferably, the Cl of (I) is replaced by H, by means of Pd in CHCl₃, and the amide is hydrolysed to the acid. The following are thus prepared: 3-acetoxy-4-methoxyphenylacetamide, m.p. 141° after softening; homoveratramide, m.p. 146—147°; homopiperonylamide, m.p. 172—173°; homoisovanillic acid, m.p. 127—128°; homoveratric acid, m.p. 98°; homopiperonylic acid, m.p. 129°. α-Chloro-3:4-dimethoxyphenylacetamide is reduced and demethoxylated by H₂ (Adams PtO₂ in AcOH) to cyclohexylacetamide, m.p. 171—172°. 6-Bromo-3:4-dimethoxyphenylacetamide has m.p. 195.5—196.5°.

H. W.

Transformation of substituted acetylmandelonitriles into α-halogenated phenylacetamides. G. HAHN, K. STEHL, and H. J. SCHULZ (Ber., 1939, 72, [B], 1291—1301).—The conversion of acetylcyanohydrins into α-chloroarylacetamides appears to be restricted to alkoxy- and certain hydroxyalkoxy-substituted acetylmandelonitriles. The mechanism of the change is discussed. *iso*Vanillin is converted by the successive action of NaHSO₃ and KCN into 3-hydroxy-4-methoxymandelonitrile, m.p. 99—100° (yield 85%), transformed by NaOAc and boiling Ac₂O into 3-acetoxy-4-methoxyacetylmandelonitrile, m.p. 85°; this is kept in C₆H₆ saturated with HCl for 3—4 days, after which the solution is evaporated to dryness on the steam-bath and the residue is kept in vac. over KOH and then dissolved in warm EtOAc, thus giving α-chloro-3-acetoxy-4-methoxyphenylacetamide, m.p. 135—136°. Vanillin similarly gives 4-hydroxy-3-methoxymandelonitrile, m.p. 83°, whence is derived 4-acetoxy-3-methoxyacetylmandelonitrile, m.p. 103—104°. 3:4-Dimethoxyacetylmandelonitrile, m.p. 78° (corr.), yields α-chloro-3:4-dimethoxyphenylacetamide (I), m.p. 145°, which is stable indefinitely when homogeneous. α-Chloro-3:4-methylenedioxyphenylacetamide, m.p. 107°, from 3:4-methylenedioxyacetylmandelonitrile, is converted by aq. NaN₃

into the α -azido-compound, m.p. 95.5—96.5°. (I) is converted by boiling MeOH into α -methoxy-, m.p. 126° (53% yield), by NH_3 in dry CHCl_3 at 100° into the very hygroscopic α -amino-, m.p. 132—134° after softening, by NHET_2 in C_6H_6 at 100° into α -diethyl-amino-, m.p. 133° (also hydrate), by NH_2Ph in boiling C_6H_6 into α -anilino-, m.p. 167—169° (yield 79%), by homoveratrylamine into α -homoveratrylamino-, m.p. 146°, by aq. NaN_3 at room temp. into α -azido-, m.p. 145°, and by KCN into α -cyano-, m.p. 151°, 3:4-dimethoxyphenylacetamide. α -Azido-3-acetoxy-4-methoxyphenylacetamide has m.p. 124°. 3:4-Dimethoxyphenylacetamide and boiling PhNCO afford *N*-homoveratroyl-*N'*-phenylcarbamide, m.p. 166°. H. W.

Common basis of intramolecular rearrangements. V. Inversion of configuration in semipinacolic deamination. Configurational relationship between (+)-alanine and (+)- α -phenylpropionic acid. H. I. BERNSTEIN and F. C. WHITMORE (J. Amer. Chem. Soc., 1939, 61, 1324—1326; cf. A., 1938, II, 408).—Curtius rearrangement of the azide of (+)- $\text{CHPhMe}\cdot\text{CO}_2\text{H}$ (I) gives (—)- $\text{CHPhMe}\cdot\text{NH}_2$ [Bz derivative, m.p. 120—121° (lit., 125.5°, 119.5°), $[\alpha]_D^{25}$ —39.2° in C_6H_6]. Together with the correlations of (I) with (—)-alanine, of (+)-alanine with (—)- $\text{NH}_2\cdot\text{CHMe}\cdot\text{CPh}_2\cdot\text{OH}$ (II), and of (I) with (+)- $\text{COPh}\cdot\text{CHPhMe}$ (III), this shows that semipinacolic deamination of (II) to (III) involves a Walden inversion, which must occur by attack of the wandering Ph at the back of the active C.

R. S. C.

Preparation of thyroxine and mono- and di-iodotyrosine from iodinated protein. W. LUDWIG and P. VON MUTZENBECHER (Z. physiol. Chem., 1939, 258, 195—211; cf. A., 1937, II, 40).—Finely divided I is added to a solution of casein in aq. NaHCO_3 at 37°; the solution is acidified and the ppt. is redissolved in NaOH and dialysed against distilled H_2O . Pptn. with $\text{EtOH}\cdot\text{AcOH}$ leads to an iodoprotein with 6—8% of organically bound I; it has marked thyroid gland activity. It is hydrolysed by alkali to a highly active fraction rich in I from which cryst. thyroxine can be isolated. The mother-liquors from the active fraction contain di- (I) and mono-iodotyrosine (+ H_2O) [hydrogenated to tyrosine and iodinated to (I)]. H. W.

Influence of solvents on the stereochemical course of addition of hydrogen bromide to monobasic acetylenic acids and relation of solvent effect to chemical structure. A. MICHAEL [with G. H. SHADINGER] (J. Org. Chem., 1939, 4, 128—138).—Aq. HBr and $\text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H}$ (I), by *cis*-addition, yield β -bromoisocinnamic acid. (I) and HBr in C_6H_6 , PhBr , or PhMe give α -bromocinnamic acid, but in MeNO_2 , PhNO_2 , EtBr , Et_2O , or COMe_2 , *trans*- β -bromocinnamic acid is formed, probably by transformation of the *cis*- β -acid; the latter is isolated after short reaction in MeNO_2 . (I) and HCl in CHCl_3 , Et_2O , or PhMe react extremely slowly at room temp. or 60°. $\text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{H}$ and HBr in H_2O or MeNO_2 give β -bromocrotonic acid, m.p. 93—94°; in C_6H_6 or PhBr , the α -Br-acid, m.p. 105—106°, is formed. Catalytic transformation of the bromoisocrotonic acids is less facile than that of the corresponding

bromocinnamic acids, and the primarily-formed Br-acids are isolated. $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and HBr , in H_2O or PhBr at room temp., or in C_6H_6 or PhMe at 60°, afford $\text{CHPhBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in H_2O or C_6H_6 at room temp. gives $\text{CHMeBr}\cdot\text{CO}_2\text{H}$. Theoretical aspects of the influence of solvent action on addition of HBr to $\alpha\beta$ -unsaturated acids are discussed. There is no direct relationship between solvent effect and the associating, dissociating, or dielectric consts. of the solvents. Markovnikov's empirical addition rule is valid solely in the Δ^1 -alkene and -alkinene series, and then only if addition is unaccompanied by migration of H or Me. A. T. P.

isoAmylamides of unsaturated acids. S. KANAO and S. INAGAWA (J. Pharm. Soc. Japan, 1938, 58, 65—67).— γ -Methyl- Δ^1 -penteno-*, b.p. 151°/7 mm., sorb., b.p. 169—170°/8 mm., m.p. ~80°, Δ^1 -undeceno-, b.p. 168—169°/4 mm., *isohexo*-, b.p. 141°/5 mm., phenylpropiol-* (I), b.p. 192—193°/8 mm., m.p. 61°, cinnam-*, m.p. 89° (previous sintering), 4-hydroxy-3-methoxycinnam-, 3:4-methylene-dioxy-cinnam-, m.p. 90—91°, β -2-furylacryl-, b.p. 197—198°/5.5 mm., m.p. ~60—61°, piper-, m.p. 138—139°, and β -phenylpropion-isoamylamide, b.p. 160°/4 mm., are prepared from the acid chloride or ester and isoamylamine. Those marked * have strong pungent tastes; (I) is the most marked. H. B.

Syntheses in the phenanthrene series. III. R. GREWE (Ber., 1939, 72, [B], 1314—1317).—2- β -Phenylethylcyclohexanone (I), Zn, and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in boiling C_6H_6 give *Et* 1-hydroxy-2- β -phenylethylcyclohexylacetate, b.p. 165°/0.2 mm. transformed by syrupy H_3PO_4 at 100° into as-octahydrophenanthryl-1-acetic acid (II), m.p. 140°, and its *Et* ester, b.p. 157°/0.2 mm. (II) is decarboxylated and dehydrogenated by Pd at ~280° to 1-methylphenanthrene, m.p. 120° (picrate, m.p. 135—136°). *Et* 2-ketocyclohexylacetate and $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{MgBr}$ give 2-hydroxy-2- β -phenylethylcyclohexylacetolactone, b.p. 190°/0.3 mm., m.p. 68°, converted by syrupy H_3PO_4 into (II). β -Phenylethylcyclohexene is transformed by BzO_2H in CHCl_3 into the oxide, converted by conc. HCl in boiling MeOH into (I). H. W.

Reactivity of atoms and groups in organic compounds. XIX. Relative reactivities of the chlorine atoms in derivatives of benzoyl chloride. J. F. NORRIS and V. W. WARE (J. Amer. Chem. Soc., 1939, 61, 1418—1420; cf. A., 1935, 1206).—The following reactivities (relative to that of BzCl) of substituted benzoyl chlorides with EtOH at 0° are recorded; *F* = very fast; *S* = very slow: *o*-*Et* 2.73; *o*-*OEt* 41.6; *o*-*F*, *m*-4.35, and *p*-*Bz* 4.31; *m*-1.04 and *p*- CH_2Ph 0.75; *m*-1.64 and *p*- CH_2Cl 1.30; 2:4-6.75 and 2:6- Me_2 *F*; 2:6-(OMe)₂ *F*; 2:4-7.7, 2:5-14.1, and 3:4- Cl_2 7.2; 2:4-31.6, 3:5-*F*, and 2:6-(NO_2)₂ *S*; 2:4:6- Et_3 *F*, $-\text{Cl}_3$ *S*, and $-\text{Br}_3$ *S*. Regularities are pointed out.

R. S. C.

Bromination of *p*-diphenyl benzoate. S. E. HAZLET, G. ALLIGER, and R. TIEDE (J. Amer. Chem. Soc., 1939, 61, 1447—1449).—Bromination of *p*-diphenyl benzoate (I) and benzenesulphonate (Hazlet, A., 1937, II, 332) occurs in the 4'-position of the Ph_2 nucleus, which does not accord with any orientation

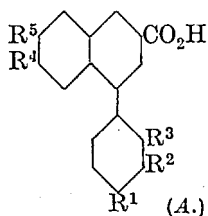
rule. Steric hindrance is considered a possible reason. 4'-Bromo-4-diphenyl benzoate, m.p. 192—193°, is prepared from (I) by Br and a trace of Fe powder in AcOH at 100° and from $p\text{-C}_6\text{H}_4\text{Br}\text{-C}_6\text{H}_4\text{-OH}\cdot p$ (II) by $\text{BzCl}\text{-C}_6\text{H}_5\text{N}$ and is hydrolysed by $\text{KOH}\text{-EtOH}$ to (II) and BzOH . $p\text{-C}_6\text{H}_4\text{Ph}\text{-OH}$ with Br (1:1 or 2:1 mols.) and a trace of Fe in AcOH at 100° gives 3-bromo-, m.p. 93.5—94.5° (benzoate, m.p. 93—94°), and 3:5-dibromo-4-hydroxydiphenyl, m.p. 93.5—94° (benzoate, m.p. 169—170.5°). R. S. C.

Condensation products of anisic acid esters, formaldehyde, and hydrochloric acid in presence of zinc chloride. S. HANAI (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 30—41).—Condensation is analogous to that of PhOMe . A. T. P.

Syntheses in the 1-arylnaphthalene group.

I. Ring-closures of the β -benzylidene- α -benzylidene-propionic acid group. T. OHMAKI (J. Pharm. Soc. Japan, 1938, 58, 4—8).—Na aroylpropionates are condensed with aromatic aldehydes in the presence of $\text{NaOH}\text{-EtOH}$ to the following γ -crotonolactones: γ -phenyl- α -benzylidene-, m.p. 150°; γ -phenyl- α -3:4-dimethoxybenzylidene-, m.p. 130°; γ -phenyl- α -3:4-methylenedioxybenzylidene-, m.p. 175°; γ -*p*-anisyl- α -benzylidene-, m.p. 178—179°; γ -*p*-anisyl- α -*p*-anisylidene-, m.p. 178°; γ -*p*-anisyl- α -*o*-acetoxymethoxybenzylidene-, m.p. 194°; γ -*p*-anisyl- α -*m*-acetoxymethoxybenzylidene-, m.p. 153°; γ -*p*-anisyl- α -4-acetoxy-3-methoxybenzylidene-, m.p. 195°; γ -*p*-anisyl- α -3:4-methylenedioxybenzylidene-, m.p. 217 (corr.); γ -3:4-dimethoxyphenyl- α -benzylidene-, m.p. 147°; γ -3:4-dimethoxyphenyl- α -*p*-anisylidene-, m.p. 143°; γ -3:4-dimethoxyphenyl- α -3:4-dimethoxybenzylidene-, m.p. 155°; γ -3:4-dimethoxyphenyl- α -4-acetoxy-3-methoxybenzylidene-, m.p. 207° (corr.); γ -3:4-dimethoxyphenyl- α -3-methoxy-4-ethoxybenzylidene-, m.p. 185°; γ -3:4-dimethoxyphenyl- α -3:4-methylenedioxybenzylidene-, m.p. 234° (corr.); γ -3:4-dimethoxyphenyl- α -*p*-tolylidene-, m.p. 154°; γ -3:4-dimethoxyphenyl- α -*m*-tolylidene-, m.p. 138°; γ -3:4-dimethoxyphenyl- α -2:4-dimethoxybenzylidene-, m.p. 186—187°; γ -2:4-dimethoxyphenyl- α -4-acetoxy-3-methoxybenzylidene-, m.p. 193°; γ -2:4-dimethoxyphenyl- α -3:4-methylenedioxybenzylidene-, m.p. 233.5° (corr.). The following propionic acids are simultaneously obtained: β -benzoyl- α -benzylidene-, m.p. 171°; β -benzoyl- α -3:4-dimethoxybenzylidene-, m.p. 171°; β -benzoyl- α -3:4-methylenedioxybenzylidene-, m.p. 198°; β -*p*-anisoyl- α -benzylidene-, m.p. 172°; β -*p*-anisoyl- α -*p*-anisylidene-, m.p. 193—194°; β -*p*-anisoyl- α -*o*-hydroxybenzylidene-, m.p. 179°; β -*p*-anisoyl- α -4-hydroxy-3-methoxybenzylidene-, m.p. 219.5° (corr.); β -*p*-anisoyl- α -3:4-methylenedioxybenzylidene-, m.p. 213° (corr.); β -3:4-dimethoxybenzoyl- α -benzylidene-, m.p. 218° (corr.); β -3:4-dimethoxybenzoyl- α -*p*-anisylidene-, m.p. 192°; β -3:4-dimethoxybenzoyl- α -3:4-dimethoxybenzylidene-, m.p. 175°; β -3:4-dimethoxybenzoyl- α -4-hydroxy-3-methoxybenzylidene-, m.p. 190°; β -3:4-dimethoxybenzoyl- α -3-methoxy-4-ethoxybenzylidene-, m.p. 189°; β -3:4-dimethoxybenzoyl- α -3:4-methylenedioxybenzylidene-, m.p. 242° (corr.); β -3:4-dimethoxybenzoyl- α -*p*-tolylidene-, m.p. 217° (corr.); β -3:4-dimethoxybenzoyl- α -*m*-tolylidene-, m.p. 189°; β -2:4-dimethoxybenzoyl- α -4-hydroxy-3-methoxybenzylidene-, m.p. 179°. MeOH saturated with HCl

or 20% $\text{H}_2\text{SO}_4\text{-MeOH}$ causes ring-closure of such of the above acids as contain OH or OMe at $\text{C}_{(3)}$ or CH_2O_2 at $\text{C}_{(3)}$ and $\text{C}_{(4)}$ of the arylidene group, giving acids (A) in which (1) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = \text{R}^5 = \text{OMe}$; (2) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 + \text{R}^5 = \text{CH}_2\text{O}_2$; (3) $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^5 = \text{OMe}$, $\text{R}^4 = \text{OH}$; (4) $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^1 = \text{OMe}$, $\text{R}^4 + \text{R}^5 = \text{CH}_2\text{O}_2$; (5) $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$, $\text{R}^1 = \text{OMe}$, $\text{R}^5 = \text{OH}$; (6) $\text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^2 = \text{R}^5 = \text{OMe}$, $\text{R}^4 = \text{OH}$; (7) $\text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{OMe}$; (8) $\text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^2 = \text{R}^5 = \text{OMe}$, $\text{R}^4 = \text{OEt}$; (9) $\text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^2 = \text{OMe}$, $\text{R}^4 + \text{R}^5 = \text{CH}_2\text{O}_2$; (10) $\text{R}^2 = \text{H}$, $\text{R}^1 = \text{R}^3 = \text{R}^5 = \text{OMe}$, $\text{R}^4 = \text{OH}$; (11) $\text{R}^2 = \text{H}$, $\text{R}^1 = \text{R}^3 = \text{OMe}$, $\text{R}^4 + \text{R}^5 = \text{CH}_2\text{O}_2$. H. W.



Fluorenones and diphenic acids. VIII. Ring-cleavage of fluorenone-4-carboxylic acids. E. H. HUNTRESS and (Miss) M. K. SEIKEL (J. Amer. Chem. Soc., 1939, 61, 1358—1364; cf. A., 1939, II, 320).—15—25% of fluorenone-4-carboxylic acid (I) is recovered unchanged after heating with KOH in Ph_2O , best at 170—180° (15 min. or 3 hr.), the remainder yielding diphenic (39%) and diphenyl-2:6-dicarboxylic acid (II) (28%), m.p. 281—282° [with cold, conc. H_2SO_4 very readily regenerates (I)]; the acids are best separated by conversion into the anhydrides and hydrolysis of the anhydride of (II) by cold 3—6*N*-NaOH. KOH- Ph_2O , best at 170—175°, gives no $m\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ derivative from 1:6-dichlorofluorenone-4-carboxylic acid (III) [best (100%) obtained from 5:5'-dichlorodiphenic acid (IV) and conc. H_2SO_4 at 100°], new m.p. 249°; the products are unchanged (III), (IV), and the dilactone (V), m.p. >350°, sublimes at 270—280°/15—20 mm., of 6:6'-dihydroxydiphenic acid. The structure of (V) is proved by conversion by $\text{Me}_2\text{SO}_4\text{-NaOH}$ into Me_2 6:6'-dimethoxydiphenate and thence (alkali) 6:6'-dimethoxydiphenic acid, m.p. 290—291.5° (lit. 288—290°, 293—294°). 1:6-Dichlorofluorenone-5-carboxylic acid (VI), new m.p. 243—244°, and KOH in Ph_2O at 180° give unchanged acid, 10—20% of 3:3'-dichlorodiphenyl-2:6-dicarboxylic acid, m.p. 236—236.5° (undergoes ring-closure rapidly in H_2SO_4 at 100°), some 5- (or 3-)hydroxy-6-carboxydiphenyl-methylolide (lactone of 3:2'-dihydroxydiphenyl-2:6-dicarboxylic acid) (VII) (best obtained by fusion for only a short time at 220°), m.p. 299—301° (decomp.), and much tar. Methylation and subsequent hydrolysis of (VII) gives 3:2'-dimethoxydiphenyl-2:6-dicarboxylic acid, m.p. 249—249.5°. 3:3'-Dichlorodiphenic acid, readily converted by conc. H_2SO_4 at room temp. into (VI), is not obtained from (VI). At most traces of decarboxylation occur during these reactions. R. S. C.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. VIII. Interaction and colour in systems containing methyl 4:6:4':6'-tetranitrodiphenate and various hydrocarbons. D. L. HAMMICK and G. SIXSMITH (J.C.S., 1939, 972—974).— Me 4:6:4':6' -tetranitrodiphenate (I), m.p. 176.1° (corr.), interacts

in the liquid phase with hydrocarbons with production of colour. Temp.-composition curves are given. By crystallisation of (I) (1 mol.) + hydrocarbon (4 mols.) from MeOH, or as a solid phase in two-component systems, the following pale yellow complexes [2 mols. of (I) to 1 mol. of hydrocarbon] are obtained: from C_6H_6 , m.p. 156° ; *o*-, m.p. 165° , *m*-, m.p. 160° , and *p*-xylene, m.p. 164° ; $C_{10}H_8$, m.p. 167.5° ; anthracene, m.p. 164° ; indene, m.p. 159.2° ; $PhNO_2$, m.p. 121° ; $m\text{-}C_6H_4(NO_2)_2$, m.p. 70° ; $s\text{-}C_6H_3(NO_2)_3$, m.p. 142.5° ; $1\text{-}C_{10}H_7\cdot NO_2$, m.p. 135° ; (*o*- $NO_2\cdot C_6H_4$)₂, m.p. 115° . Acenaphthene gives a deep yellow 1:1 complex, m.p. 163° . PhMe, $s\text{-}C_6H_3Me_3$ (II), Ph_2 , *pp'*-ditolyl, CH_2Ph_2 , $CHPh_3$, C_6Me_6 , and (*p*- $NO_2\cdot C_6H_4$)₂, do not afford solid complexes. In the system with PhMe, the liquid components tend to separate into coloured liquid layers, and with (II) actually separate. A. T. P.

Lichen substances. XCI. Usnic acid. VI. Y. ASAHINA and M. YANAGITA (Ber., 1939, 72, [B], 1140—1146).—Treatment of *d*-usnic acid (I) with Ac_2O containing a little conc. H_2SO_4 at 90° gives *dl*-diacetylusnic acid (II), m.p. $205\text{--}207^\circ$, converted by 10% Na_2CO_3 into *dl*-monoacetylusnic acid, m.p. 191° . Boiling 95% EtOH converts (II) or the Ac_2 derivative of (I) into *diacetylusnic acid ethoxylate*, $C_{24}H_{26}O_{10}$, m.p. $88\text{--}89^\circ$, transformed by boiling 60% AcOH into *Et diacetylacetusetate*, m.p. 125° , which affords Et acetusetate (III), m.p. 150° , when pptd. from conc. H_2SO_4 by H_2O . Boiling 60% AcOH transforms di- into mono-acetylusnetol. Boiling Ac_2O converts *l*-dihydrousnic acid into its Ac_2 derivative, m.p. 150° , whereas (III) and Ac_2O at $90\text{--}95^\circ$ yield Et monoacetylacetusetate. With resorcinol or $\alpha\text{-}C_{10}H_7\cdot OH$ and conc. H_2SO_4 at 0° (III) affords products, $C_{22}H_{18}O_7\cdot EtOH$, m.p. 295° (decomp.) after becoming discoloured at $\sim 275^\circ$, and $C_{26}H_{20}O_8$, m.p. 272° , which is unchanged by boiling 50% KOH. Conc. aq. NH_3 converts (I) in boiling $C_6H_6\text{-}EtOH$ into *d*-usnamide, m.p. 251° , $[\alpha]_D^{25} + 407.32^\circ$ in $CHCl_3$, transformed by boiling 80% AcOH into a substance, $C_{18}H_{16}O_7$, m.p. 199° , $[\alpha]_D^{25} + 454.3^\circ$ in $CHCl_3$. *l*-Usnamethylamide, m.p. $209\text{--}209.5^\circ$, $[\alpha]_D^{25} + 384.3^\circ$ in $CHCl_3$, is unchanged by boiling 80% AcOH. Freshly prepared *d*-usnanilide had m.p. (varying) $140\text{--}160^\circ$; in a few months it passes into the stable modification, m.p. 170° , $[\alpha]_D^{25} + 273.9^\circ$ in $CHCl_3$. It is transformed by cold, conc. H_2SO_4 into *anilinousnic acid*, m.p. $223\text{--}225^\circ$, converted by boiling 80% AcOH into decarbousnic acid and reduced (Pd-C in AcOH) to *dihydroanilinousnic acid*, m.p. 207° (softens $\sim 180^\circ$). *d*-Dihydrousnamide, m.p. 202° , $[\alpha]_D^{25} + 222.2^\circ$ in $CHCl_3$, is prepared from the *l*-acid. H. W.

Structural analysis and chemical linkings. V. Structure of molecular lattices determined by means of Fourier analysis. V. CAGLIOTTI and G. GIACOMELLO (Gazzetta, 1939, 69, 245—254).—The structure of the complex between palmitic acid and deoxycholic acid is determined. Structural analogies with inorg. complexes are discussed.

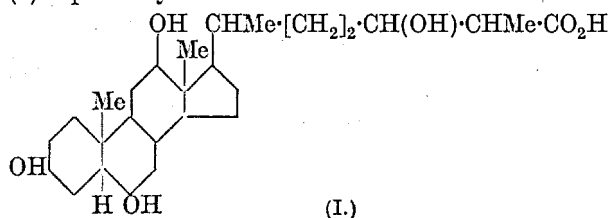
O. J. W.

Relation between methyl ætiodeoxycholate and the methyl dihydroxyætiodeocholane derived from digoxigenin. Methyl 12-epiætiodeoxycholate. H. L. MASON and W. M. HOEHN (J. Amer. Chem. Soc.,

1939, 61, 1614—1615).—Hydrogenation (PtO_2 ; EtOH) of Me 3:12-diketoætiodeocholane gives a mixture of esters; removal of the esters having β -configuration at C_{12} as digitonides, followed by adsorption on Al_2O_3 , gives *Me epiætiodeoxycholate*, m.p. $176\text{--}178^\circ$, $[\alpha]_D^{25} + 49.4 \pm 2.4^\circ$ in EtOH (3-benzoate, m.p. $136\text{--}138^\circ$, $[\alpha]_D^{25} + 62 \pm 3^\circ$), identical with the ester, $[\alpha]_D^{25} + 45.6 \pm 3^\circ$, $[\alpha]_D^{25} + 38.9 \pm 3^\circ$ in MeOH, obtained from digoxigenin, which thus has at C_{12} a OH differing sterically from that of deoxycholic acid (cf. A., 1939, II, 27). R. S. C.

Sterols. LXIII. Ætiodeocholic acids from the pregnanediols. R. E. MARKER and E. L. WITTE (J. Amer. Chem. Soc., 1939, 61, 1329—1332).—Pregnan-3(α)-ol-20-one with PhCHO and NaOEt in EtOH at $25\text{--}30^\circ$ gives the 21-CHPh derivative (I), m.p. $230\text{--}232^\circ$, the acetate, m.p. 152° , of which is oxidised by CrO_3 in warm AcOH to acetylætiolithocholic acid, m.p. $230\text{--}232^\circ$, and BzOH; ætiolithocholic acid, prepared therefrom by hot 2% KOH-EtOH, has m.p. $275\text{--}276^\circ$, and yields (CrO_3) 3-keto-ætiodeocholic acid, m.p. $246\text{--}249^\circ$. With CrO_3 in AcOH at 25° , (I) or 21-benzylidenepregnan-3(β)-ol-20-one (similarly prepared), m.p. 179° (acetate, m.p. 175°), gives 21-benzylidenepregnane-3:20-dione, m.p. $212\text{--}214^\circ$, which could not be obtained from pregnane-3:20-dione. The acetate, m.p. $207\text{--}209^\circ$, of 21-benzylidenecallopregnan-3(β)-ol-20-one, m.p. $185\text{--}187^\circ$, is similarly prepared and oxidised by CrO_3 in AcOH at 100° to 3(β)-acetoxyætiodeocholic acid, m.p. $247\text{--}249^\circ$, which gives the OH-acid, m.p. $250\text{--}252^\circ$. R. S. C.

Tetrahydroxynorsterocholic acid from the bile of the "gigi" fish (Pelteobagrus nudiceps). K. OHTA (Z. physiol. Chem., 1939, 259, 53—61).—Hydrolysis (1% KOH at 135°) of the bile yields taurine, cholic acid (yield in winter 0.3%, summer 0.1%), and tetrahydroxynorsterocholic acid (I), $C_{27}H_{46}O_8$ (less probably $C_{28}H_{48}O_8$) (yield in winter 0.33%, summer 1.11%), m.p. $212\text{--}214^\circ$, $[\alpha]_D^{25} + 27.24^\circ$ in abs. EtOH (Me, m.p. 204° , and Et ester, m.p. $217\text{--}218^\circ$). Oxidation of (I) in $COMe_2$ with 10% aq. $KMnO_4$ gives an isocholic (trihydroxycholic) acid, $C_{24}H_{40}O_5$, sinters 189° , m.p. $207\text{--}208^\circ$, whilst $CrO_3\text{-}AcOH$ gives α -triketocholic acid (II), $C_{24}H_{34}O_5$, m.p. 198° [Me ester, m.p. $173\text{--}174^\circ$ (oxime, decomp. $226\text{--}227^\circ$)], and the isomeric β -triketocholic acid (III), m.p. 234° [Me ester, m.p. $206\text{--}207^\circ$ (oxime, decomp. 239°)]. (II) boiled with Na_2CO_3 gives (III). Clemmensen reduction of (II) gives allocholic acid. (I) is probably as shown.



W. McC.

Sterols. LXVI. Reactions of tigogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 1516—1517).—Tigogenin (I) probably has the same type of side-chain as sarsasapogenin, but

differs in being more slowly reduced by Zn-Hg-EtOH-HCl [in poor yield to a substance, (?) $C_{27}H_{46}O_2$, m.p. 152° (digitonide), which absorbs Br in AcOH but is unchanged by H_2 -PtO₂ in Et₂O]. SeO₂ oxidises (I); H_2 -PtO₂ in AcOH at 70°/3 atm. reduces it to *dihydrotigogenin*, m.p. 167—168° (stable to Br and SeO₂; digitonide; *dibenzoate*, m.p. 110—112°), oxidised by CrO₃ in AcOH to an acid, $C_{27}H_{42}O_4$, m.p. 192°. Tigogenin acetate and Br in AcOH containing a trace of HBr give *bromotigogenin acetate*, m.p. 223° (decomp.) (stable to SeO₂), reduced to (I) by Na-EtOH. Tigogenone [but not (I)] and Zn in HCl-EtOH give *deoxytigogenin*, $C_{27}H_{44}O_2$, m.p. 173—174°, hydrogenated (PtO₂; AcOH-EtOH; 25°/3 atm.) to the H_2 -derivative, m.p. 92.5°. Dihydrosiosgenin is probably identical with (I), and dioscoreasapogenin identical with or very similar to diosgenin.

R. S. C.

Preparation and properties of aldehydes containing deuterium in the functional group. A. F. THOMPSON, jun., and N. H. CROMWELL (J. Amer. Chem. Soc., 1939, **61**, 1374—1376).—In presence of Pd-BaSO₄, poisoned by S and quinoline, D₂ reduces BzCl and p -C₆H₄Ph·COCl in xylene to *benzdeuteri-aldehyde* and *p*-phenylbenzdeuteri-aldehyde, isolated as NaHSO₃ compounds. The products are not pure, as the Pd causes dilution of the D₂ by H₂ by interchange with the xylene. The NaHSO₃ compounds, but not the aldehydes, lose D to H₂O.

R. S. C.

Synthesis of aromatic aldehydes. S. AKABORI and Y. SENOH (Bull. Chem. Soc. Japan, 1939, **14**, 166—168; cf. A., 1926, 957).—With formylpiperidine and POCl₃ or PCl₃ at room temp., then at 100°, PhOMe yields p -OMe·C₆H₄·CHO, and veratrole yields veratraldehyde (*semicarbazone*, m.p. 179.5°). m -C₆H₄(OMe)₂ and NEt₂·CHO similarly yield 3:4:1-C₆H₃(OMe)₂·CHO (*oxime*, m.p. 103—104°). The method is not suitable for free phenols. A. LI.

Reactions of N-chloroaldimines with Grignard reagents. J. W. LEMAISTRE, A. E. RAINSFORD, and C. R. HAUSER (J. Org. Chem., 1939, **4**, 106—110; cf. A., 1935, 620; 1936, 332).—CHR:NCl (I) and MgR'Br (II) react thus: (a) (II) removes HCl from (I) to give RCN (and R'H), (b) forming CHR:N·MgBr and R'Cl. MgEtBr added slowly to o -C₆H₄Cl·CH:NCl in Et₂O at -45° gives o -C₆H₄Cl·CN (13) and o -C₆H₄Cl·CH:N·MgBr (43% yield). Similarly, MgEtBr and p -OMe·C₆H₄·CH:NCl at 0° give p -OMe·C₆H₄·CN (17) and p -OMe·C₆H₄·CH:N·MgBr (50%). p -C₆H₄Cl·CH:NCl (III) and MgEtBr at 0° or 23—28° afford p -C₆H₄Cl·CN (IV) (20 or 34) and p -C₆H₄Cl·CH:N·MgBr (V) (45 or 45%), respectively. (III) and MgPhBr or p -C₆H₄Cl·MgBr (VI) at 0° give (IV) (10 or 5) and (V) (61 or 18%), respectively; PhCl and p -C₆H₄Cl₂ are also obtained in the reaction with (VI). LiPh (method: Gilman *et al.*, A., 1932, 519) and (III) give (IV) (20%) and a N-Li compound, hydrolysed to p -C₆H₄Cl·CHO (34%). Mechanisms of reactions are discussed.

A. T. P.

Velocity of formation of oximes, semicarbazones, and phenylhydrazones.—See A., 1939, I, 423.

Condensation of alcohols, ethers, and esters with aromatic hydrocarbons in the presence of aluminium chloride. J. F. NORRIS and B. M. STURGIS (J. Amer. Chem. Soc., 1939, **61**, 1413—1417).—With AlCl₃ at room temp., MeOH, EtOH, and PhOH give compounds, AlCl₃·ROH, but, when heated, give AlCl₂·OR and then good yields of alkyl chlorides. C₆H₆ is thus alkylated by the alcohols if an excess of AlCl₃ is used. PhBu' is similarly obtained from Bu'OH in 84% yield. Et₂O is cleaved into EtCl and affords under suitable conditions 36% of PhEt with very little polyalkylated product. Esters are generally cleaved into RCl and RCOCl. Thus, EtOAc gives mainly COMe·C₆H₃Et₂ with some PhEt and COPhMe. With C₆H₆ (4 mols.) and 1 mol. of AlCl₃, PhOAc gives *o*- and *p*-OH·C₆H₄·COMe and PhOH, or, if more AlCl₃ is used, 43—60% of COPhMe at the expense of the OH·C₆H₄·COMe. PhOAc (1 mol.), PhMe (4), and AlCl₃ (2 mols.) give 82% of *o*- and *p*-C₆H₄Me·COMe. AlCl₃·OPh with AcCl gives phenacetin (Bülow, A., 1903, i, 357), *o*- and *p*-OH·C₆H₄·COMe, with or without PhOAc according to the conditions; with AcOH it gives the same products and some Ph₂O. *o*-NO₂·C₆H₄·OAc, C₆H₆, and AlCl₃ give 82% of COPhMe. NH₂Ac and AlCl₃ give 60% of MeCN. PhCN is obtained in 84 and 50% yield from NH₂Bz and NH₄OBz, respectively, by AlCl₃.

R. S. C.

Oximes. I. Ketoxime N-methyl ethers. J. MEISENHEIMER and L. H. CHOU. II. Beckmann change. XI. J. MEISENHEIMER and N. CAMPBELL. III. Constitution of oximes. II. J. MEISENHEIMER and G. GAISER. IV. Stereoisomeric oximes of p-dimethylaminobenzophenone. J. MEISENHEIMER and A. KAPPLER (Annalen, 1939, **539, 78—92, 93—95, 95—99, 99—102; cf. A., 1929, 566).—I. COArAlk do not react with NHalk·OH, unless the Ar has OH *o*- or, less well, *p*- (not *m*-) to the CO (cf. A., 1932, 743). COPhMe, COPh₂, m -NO₂·C₆H₄·COMe, 2:1-OMe·C₁₀H₆·COMe, and m -OH·C₆H₄·COMe do not react with NHMe·OH. Prep. of PhOAc, b.p. 84—85°/15 mm., NHMe·OH, HCl (I), p -C₆H₄Me·OAc, b.p. 108—110°/23 mm., 4:1:3-OH·C₆H₃Me·COMe (II), α - (III), m.p. 46°, and β -C₁₀H₇·OAc, m.p. 70°, and 2:1-OH·C₁₀H₆·COMe, m.p. 46°, is described. PhOAc and AlCl₃ at 175° give 60% of *p*-, m.p. 108° (lit. 112°), and 25% of *o*-OH·C₆H₄·COMe (IV), b.p. 101—102°/17 mm. With AlCl₃ in PhNO₂, (III) gives 26% of 1:2-, m.p. 99—100°, and 22% of 4:1-OH·C₁₀H₆·COMe, m.p. 198°. With NaOEt in EtOH, (IV) and (I) give 15% of *o*-hydroxyacetophenoxime N-Me ether, m.p. 89—90°; with NaOAc in abs. EtOH a substance, C₁₆H₁₆O₂N₂, m.p. 196° (no FeCl₃ colour), insol. in acid or alkali, is also formed. Similarly, (II) gives 2-hydroxy-5-methylacetophenoxime N-Me ether, m.p. 123—124°, with or without a substance, C₁₈H₂₀O₂N₂, m.p. 223°. By condensation in presence of NaOAc in abs. EtOH are obtained 2- (V), m.p. 224—225° (picrate, m.p. 156—157°), and 4-hydroxy-1-naphthyl Me ketoxime N-Me ether, m.p. 238° (decomp.). Condensation in presence of NaOEt gives 1-hydroxy-2-naphthyl Me ketoxime N-Me ether (VI), m.p. 133—134°, and *p*-hydroxyacetophenoxime N-Me ether, m.p. 205° (decomp.). H₂-**

PtO₂ in AcOH reduces (V) to α -2-hydroxy-1-naphthylethylmethylamine (*picrate*, m.p. 157°; *hydrochloride*, m.p. 150°), and (VI) to α -1-hydroxy-2-naphthylethylmethylamine (*picrate*, +2MeOH, m.p. ~150°, resolidifies, decomp. ~200°); Zn-AcOH and Sn-HCl are without effect in the cold, and, when heated, cause decomp.

II. Other data in the lit. show that the configuration assigned by von Auwers *et al.* (A., 1931, 223) to Ph styryl ketoxime is incorrect and should be *syn*. This is supported by reaction with KMnO₄ in COMe₂ at 0° to give 72% of 3 : 5-diphenylisooxazole (stable to KMnO₄) with some PhCHO and BzOH.

III. α -*p*-Nitrobenzophenoxime (A., 1925, i, 43; 1931, 1156), m.p. 159°, and PCl₅ in cold Et₂O give 94% of *p*-NO₂·C₆H₄·CO·NHPh + *p*-NO₂·C₆H₄·CO₂H. The β -oxime, m.p. 136° [*Ac* derivative, m.p. 86°, hydrolysed by alkali to the β -oxime; *carbanilido*-derivative, m.p. 170° (decomp.)], gives 90% of *p*-NO₂·C₆H₄·NHBz + *p*-NO₂·C₆H₄·NH₂ + BzOH.

The substantially unidirectional rearrangements finally disprove Swientoslawski's theory (A., 1920, i, 336; 1924, i, 645; 1929, 1290; 1932, 51) and show

Ph·C·R and *anti* (A, R = *p*-NO₂·C₆H₄) configuration, HO·N respectively. *p*-NO₂·C₆H₄·COPh is obtained

(A.) from pure *p*-NO₂·C₆H₄·COCl, C₆H₆, and AlCl₃ with, but not without, POCl₃ (best, 1 mol.).

IV. *p*-NMe₂·C₆H₄·COPh gives *oximes*, m.p. 176° (*hydrochloride*, m.p. 172°), unstable when kept, and 163°, stable when kept, which with PCl₅ in CHCl₃ at 0° give *p*-NMe₂·C₆H₄·NHBz, m.p. 228°, and *p*-NMe₂·C₆H₄·CO·NHPh, respectively, and thus have *anti* (A, R = *p*-NMe₂·C₆H₄) and *syn* configurations, respectively. The oxime, m.p. 152—154°, of G.P. 167,053 was a mixture. NPhMe₂, *p*-C₆H₄·Me·CO·NHPh, and POCl₃ at 80° and later at 150° give 4-dimethylamino-4'-methylbenzophenone, m.p. 114·5°.

R. S. C.

Reduction of α -ketol esters. L. S. BIRNBAUM and G. POWELL (J. Org. Chem., 1939, 4, 139—141).— α : 3 : 4-Triacetoxyacetophenone and Zn dust-AcOH at 40° or 90° give 3 : 4-diacetoxyacetophenone (I), m.p. 87° (*semicarbazone*, m.p. 212—213°), and not α : 3 : 4-triacetoxyethylbenzene as stated by Voswinkel (A., 1910, i, 42). (I) and aq. Na₂CO₃ or aq. H₂SO₄ give 1 : 3 : 4-C₆H₃Ac(OH)₂; a synthetic specimen of the latter and Ac₂O afford (I). COPh·CH₂·OAc is similarly reduced to COPhMe.

A. T. P.

γ -Substitution in the resorcinol nucleus. IV. Gattermann reaction with polyhydroxyacetophenones. H. A. SHAH and R. C. SHAH (J.C.S., 1939, 949—951; cf. A., 1939, II, 115).—2 : 4 : 5 : 1-(OH)₂C₆H₂Et·COMe with Zn(CN)₂·AlCl₃·HCl (*loc. cit.*) gives 2 : 4-dihydroxy-3-aldehydo-5-ethoxyacetophenone, m.p. 77—78° [2 : 4-dinitrophenylhydrazone, m.p. 261° (decomp.); *dioxime*, m.p. 189—190°], converted by CH₂Ac·CO₂Et (+ piperidine) into 5-hydroxy-3 : 6-diacetyl-8-ethylcoumarin, m.p. 189—190°, or by CN·CH₂·CO₂H—20% aq. NaOH into 5-hydroxy-6-acetyl-8-ethylcoumarin-3-carboxylic acid, m.p. 208—209° (decomp.). 6-Methylresacetophenone gives 2 : 4-dihydroxy-3-aldehydo-6-methylacetophenone (I), m.p. 98—99° [2 : 4-dinitrophenylhydr-

azone, m.p. 275° (decomp.)], and thence 5-hydroxy-6-acetyl-7-methylcoumarin-3-carboxylic acid, m.p. 220—222° (decomp.). (I) is reduced (Clemmensen) to 2 : 5-dimethyl-4-ethylresorcinol, m.p. 95—97°. 2 : 1 : 3-C₆H₃Ac(OH)₂ affords 2 : 6-dihydroxy-3-aldehydoacetophenone (II), m.p. 105—106° (*anil*, m.p. 185°), converted by CN·CH₂·CO₂H or CH₂(CO₂Et)₂ (+ piperidine) into 7-hydroxy-8-acetylcoumarin-3-carboxylic acid, m.p. 200—201° (decomp.), or its *Et* ester, m.p. 158—159°, respectively. (II) and CH₂Ac·CO₂Et afford 7-hydroxy-3 : 8-diacetylcoumarin, m.p. 166—167° (*acetate*, m.p. 170—177°). (II) is reduced (Clemmensen) to 4-methyl-2-ethylresorcinol (*di-p-nitrobenzoate*, m.p. 174—175°).

1 : 2 : 4 : 6-C₆H₂Ac(OH)₃ (method, *loc. cit.*) gives 2 : 4 : 6-trihydroxy-3-aldehydoacetophenone, m.p. 180—182° [2 : 4-dinitrophenylhydrazone, m.p. 283° (decomp.)], but 1 : 2 : 3 : 4-C₆H₂Ac(OH)₃ (unreactive 5-position; cf. A., 1939, II, 22), 5-nitroresacetophenone, and isopaeonol do not react.

A. T. P.

Reactions of bromomagnesium enolates of mesityl ketones. I. R. C. FUSON, C. H. FISHER, G. E. ULLYOT, and W. O. FUGATE (J. Org. Chem., 1939, 4, 111—118).—*iso*Butyrylmesitylene (I), its 3 : 5-Br₂-derivative (II), or α -dibromoacetylmesitylene (III) reacts with MgEtBr to give \cdot O·MgBr derivatives, converted by BzCl into the *enol benzoates*, m.p. 87—88°, 109—109·5°, and 73—74·5°, of (I), (II), and (III), respectively; no diketone is formed. The *enol acetate* and 2 : 4 : 6-trimethylbenzoate of (II) have m.p. 77—78° and 113—114°, respectively. Mesityl ketones of type C₆H₂Me₃·CO·CHR₂ (R = Me, Br) thus show a pronounced tendency to enolise. The \cdot O·MgBr derivative of (I) and PhCHO give β -(2 : 4 : 6-trimethylbenzoyl)- α -phenyl- β -methylpropan- α -ol, m.p. 85—85·5°, oxidised by CrO₃-AcOH to α -benzoyl*isobutyrylmesitylene*, m.p. 100—100·2° (*semicarbazone*, m.p. 151—152·5°). Similarly, propionylmesitylene (IV) affords β -(2 : 4 : 6-trimethylbenzoyl)- α -phenylpropan- α -ol (V), m.p. 94·5—96°, and (VIII) (below). (V) is oxidised to α -benzoylpropionylmesitylene (VI), b.p. 183—184·5°/3 mm., purified through the Cu derivative. (IV) appears to undergo C-acylation. Its MgBr derivative and BzCl give the *enol benzoate* (VII), C₆H₂Me₃·C(OBz)·CBzMe, m.p. 95·5—96°, of (VI), hydrolysed by NaOH-EtOH to BzOH and (VI), which is probably an intermediate in the formation of (VII). (VI) and aq. KOH-MeOH give BzOH and (IV) (nitration affords 3 : 5-dinitro-2 : 4 : 6-trimethylbenzoic acid). Benzylidenepropionylmesitylene (VIII), b.p. 178—180°/3 mm., and Br·CHCl₃-CCl₄ (cold) give the *dibromide*, m.p. 134—139°.

A. T. P.

p-Thiocyanophenylhydrazine. VI. [Friedel-Crafts reaction with derivatives of diphenyl ether.] Z. HORII and T. KINOCHI. VII. Z. HORII (J. Pharm. Soc. Japan, 1938, 58, 293—295, 295—296).—VI. 2 : 4 : 1-(NO₂)₂C₆H₃·OPh with AcCl and AlCl₃ gives 2 : 4-dinitro-4'-acetyldiphenyl ether, m.p. 137—137·5° (*p*-thiocyanophenylhydrazine, m.p. 168°), also obtained from 1 : 2 : 4-C₆H₃Cl(NO₂)₂ and *p*-COMe·C₆H₄·OK, oxidised (CrO₃, AcOH) to 2 : 4-dinitro-4'-carboxydiphenyl ether, m.p. 255—256°. o-C₆H₄Me·OPh and AlCl₃ with 1 or 2 mols. of AcCl

afford 4-acetyl-, b.p. 205—207°/21 mm. (*p*-thiocyanophenylhydrazine, m.p. 167—168°), or 4:4'-diacetyl-2-methyldiphenyl ether, b.p. 259—260°/17 mm., m.p. 63.5—64.5° (*p*-thiocyanophenylhydrazine, m.p. 187—188°), respectively, also prepared from 1:3:4-COMe·C₆H₃Me·OK and PhBr at 200°/5 hr. or *p*-C₆H₄Br·COMe (I), respectively. 4'-Acetyl-2-, b.p. 196°/15 mm., -3-, b.p. 204—207°/15 mm., m.p. 48—49°, and -4-methyldiphenyl ether, m.p. 53—54° (*p*-thiocyanophenylhydrazones, m.p. 107—108°, 124—125°, and 153—154°, respectively), are prepared from (I) and C₆H₄Me·OK in presence of Cu-bronze. 4-Hydroxy-2-, m.p. 128°, and -3-methyl-, m.p. 108—109°, and 2-hydroxy-4-, b.p. 245°/760 mm., and -5-methyl-acetophenone, m.p. 50°, give *p*-thiocyanophenylhydrazones, m.p. 110—111°, 185.5—187°, 185—186°, and 172.5—173.5°, respectively.

VII. 2:4-Dinitro-3'-acetyl-, m.p. 99—100°, -4'-propionyl-, m.p. 135.5—136.5°, and -4'-acetyl-2'-methyl-diphenyl ether, m.p. 119—120° (*p*-thiocyanophenylhydrazones, m.p. 146—147°, 171.5—172.5°, and 169—170°, respectively), are new. 1:2:4-C₆H₃Cl(NO₂)₂ and *o*-OH·C₆H₄·COMe in EtOH-KOEt give only 2:4:1-(NO₂)₂C₆H₃·OH; similarly *o*-C₆H₄Me·OH or *o*-OH·C₆H₄·CO₂Me affords small yields, whilst the *m*- and *p*-derivatives give good yields, of the appropriate diphenyl ethers. 2:4-Dinitro-2'-, m.p. 91—92°, -3'-, m.p. 71—72°, and -4'-methyl-, m.p. 93—94°, and -2'-, m.p. 92.5—93.5°, -3'-, m.p. 126—127°, and -4'-carbomethoxy-diphenyl ether, m.p. 145.5—146.5°, are described. *p*-Thiocyanophenylhydrazones of the following are prepared: 2-, m.p. 105—106°, and 4-, m.p. 152.5—153.5°, -nitro-4'-aldehydo-, 2:4-dinitro-3'-, m.p. 170—171°, and -4'-, m.p. 185—186°, -aldehydo-, and 2:4-dinitro-4'-aldehydo-2'-methoxy-diphenyl ether, m.p. 166.5—167.5°; *m*-hydroxy-, m.p. 151.5°, and 2:6-dihydroxy-, m.p. 146.5—147.5°, -acetophenone; *p*-C₆H₄(CHO)₂, decomp. 235°. H. B.

Chalkones: reactivity of phenyl *p*-benzyloxy-styryl ketones. S. N. RAO and T. S. WHEELER (J.C.S., 1939, 1004—1005).—*p*-Tolyl, m.p. 111°, and *o*-hydroxyphenyl *p*-benzyloxystyryl ketone (I), m.p. 115° (acetate, m.p. 105—107°), prepared from the corresponding acetophenone and *p*-CHO·C₆H₄·O·CH₂Ph, are halogenated in CHCl₃ or AcOH to give *p*-tolyl αβ-dichloro- (II), m.p. 174°, and -dibromo-β-*p*-benzyloxyphenylethyl ketone (III), m.p. 160°, and *o*-hydroxyphenyl αβ-dibromo-β-*p*-benzyloxyphenylethyl ketone (IV), m.p. 153° [acetate (V), m.p. 114°], respectively. (II) and MeOH or EtOH (+C₆H₆), refluxed for 2 hr., give *p*-tolyl α-chloro-β-methoxy-, m.p. 119°, or -ethoxy-β-*p*-benzyloxyphenylethyl ketone, m.p. 140°, respectively. Similarly prepared from (III) are *p*-tolyl α-bromo-β-methoxy-, m.p. 125°, and -ethoxy-, m.p. 145°, and [from (IV)], *o*-hydroxyphenyl α-bromo-β-methoxy- (VI), m.p. 103°, and -ethoxy-β-*p*-benzyloxyphenylethyl ketone, m.p. 102° [also from (V) and EtOH]. (III) refluxed in aq. COMe₂ for 1 hr. gives *p*-tolyl α-bromo-β-hydroxy-β-*p*-benzyloxyphenylethyl ketone, m.p. 125°. (II) and (III), refluxed with C₅H₅N, afford *p*-tolyl α-chloro-, m.p. 116°, and -bromo-*p*-benzyloxystyryl ketone, m.p. 126°, respectively. (IV) or (VI) refluxed with KCN-

EtOH affords 4'-benzyloxyflavone, m.p. 190°, converted by HBr-AcOH into 4'-hydroxyflavone, new m.p. 270°. (I) and KOH-EtOH-H₂O₂ give 4'-benzyloxyflavonol, m.p. 175—176°. (VI) and aq. KOH give 1-*p*-benzyloxybenzylidenecoumaran-2-one, m.p. 202° (dibromide, m.p. 156°), which with CH₂Ac·CO₂Et and EtOH-NaOEt affords a substance, probably $\text{O}-\text{CH}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph})\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CH}-\text{CO}-\text{CH}\cdot\text{CO}_2\text{Et}$, m.p. 156°.

A. T. P.

Fission of ketosulphidocarboxylic acids. III. Alkaline hydrolysis of ketosulphidocarboxylic acids and its dependence on the structure of the molecule. O. BEHAGHEL and H. RATZ (Ber., 1939, 72, [B], 1257—1281; cf. A., 1935, 1237).—COPh·CH₂Br and *o*-SH·C₆H₄·CO₂Na in boiling 80% EtOH yield *o*-phenacylthiolbenzoic acid, m.p. 177°, transformed by boiling 2N-NaOH into a little (*o*-CO₂H·C₆H₄·S)₂ and an unidentified liquid. *m*-Phenacylthiolbenzoic acid, m.p. 142°, is unchanged by protracted boiling with 2N-NaOH. *p*-Methylphenacylthiolacetic acid, m.p. 115—116°, and 2N-NaOH give OH·S·CH₂·CO₂H, *p*-C₆H₄Me·COMe, and a little (?) 4:4'-dimethyldiphenacylacetic acid, m.p. 174°. *p*-Ethoxyphenacylthiolacetic acid, m.p. 96° after softening, is converted by 2N-NaOH into *p*-C₆H₄Ac·OEt and 4:4'-diethoxydiphenacylacetic acid, m.p. 160—162°. The ω-Br-derivative of 3:4:1-NO₂·C₆H₃(OMe)·COMe (best obtained from *o*-NO₂·C₆H₄·OMe, AcCl, and AlCl₃ in PhNO₂ at 0°) yields 3-nitro-4-methoxyphenacylthiolacetic acid, m.p. 136—137°, converted into non-homogeneous products by 2N-NaOH. Impure α-methylphenacylthiolacetic acid, an oil, loses CO₂ when distilled in vac. and is transformed by boiling 2N-NaOH into COPhEt and OH·S·CH₂·CO₂H. A similar fission is observed with (impure) α-ethylphenacylthiolacetic acid. *o*-α-Methyl-, m.p. 136°, and -ethyl-, m.p. 136—138°, -phenacylthiolbenzoic acids are scarcely affected by boiling 2N-NaOH. *m*-Benzylthiolbenzoic acid (I) has m.p. 128—129°. CH₂Ph *o*-benzylthiolbenzoate, m.p. 113—114°, is obtained from *o*-SH·C₆H₄·CO₂H, CH₂PhCl, and Na₂CO₃ (1:2:1 mol.) in EtOH. *m*-Desylthiolbenzoic acid, m.p. 137—138°, and boiling 2N-NaOH rapidly give Bz₂, CH₂PhBz (I), (*m*-CO₂H·C₆H₄·S)₂, and BzOH. *p*-C₆H₄Me·CO·CH₂Ph (II) and Br in AcOH at 50—60° afford α-bromo-*p*-methyldeoxybenzoin, m.p. 86—87°, transformed by SH·CH₂·CO₂H and Na₂CO₃ in aq. EtOH into *p*-toluoylbenzylthiolacetic acid, m.p. 116°, which gives OH·S·CH₂·CO₂H and (II) with alkali. *o*-*p*'-Toluoylbenzylthiolbenzoic acid, m.p. 202°, and alkali yield *p*-C₆H₄Me·CO₂H and *o*-CH₂Ph·S·C₆H₄·CO₂H. *m*-*p*'-Toluoylbenzylthiolbenzoic acid, m.p. 174—176°, gives (II), *p*-C₆H₄Me·CO₂H, and (I). *p*-OEt·C₆H₄·CO·CH₂Ph (III), m.p. 105—106°, best obtained by addition of AlCl₃ followed by PhOEt to CH₂Ph·COCl in PhNO₂, gives successively α-bromo-*p*-ethoxydeoxybenzoin, m.p. 96°, and *p*-ethoxybenzoylbenzylthiolacetic acid, m.p. 106—108°, immediately hydrolysed by 2N-NaOH to (III). *o*-*p*'-Ethoxybenzoylbenzylthiolbenzoic acid, m.p. 177°, is readily transformed by boiling 2N-NaOH into *p*-OEt·C₆H₄·CO₂H, and *o*-CH₂Ph·S·C₆H₄·CO₂H. 3-Nitro-4-methoxydeoxybenzoin (IV), m.p. 132—133°, from CH₂Ph·COCl, *o*-NO₂·C₆H₄·OMe, and AlCl₃ in

PhNO₂, is converted by successive treatments with Br in AcOH and SH·CH₂·CO₂Na into 3-nitro-4-methoxybenzoylbenzylthiolacetic acid, m.p. 129—130° converted by 2N-NaOH into (IV) and OH·S·CH₂·CO₂H. o-3-Nitro-4-methoxybenzoylbenzylthiolbenzoic acid, m.p. 191°, gives 3:4:1-NO₂·C₆H₃(OH)·CO₂H and o-CH₂Ph·S·C₆H₄·CO₂H. 4-Methoxy-3-methyldeoxybenzoin, m.p. 69—70°, affords o-4-methoxy-3-methylbenzoylbenzylthiolbenzoic acid, m.p. 200°; similarly 4-methoxy-2-methyldeoxybenzoin, m.p. 75—76°, yields o-4-methoxy-2-methylbenzoylbenzylthiolbenzoic acid, m.p. 130—131°. Unrecognised products are obtained from both acids by the action of alkali. α-Benzoylbenzylthiolacetic acid, m.p. 135—136°, yields BzOH, CHPh₂Bz, and CHPh₂·S·CH₂·CO₂H when treated with alkali. 4:1-C₁₀H₆MeAc is converted by successive treatments with Br in CHCl₃ and SH·CH₂·CO₂Na into 4-methoxy-1-naphthoilmethylthiolacetic acid, m.p. 113—115°, converted by alkali into an unidentified product, m.p. 165°. 4-Methoxy-1-naphthyl CH₂Ph ketone, m.p. 83—84°, from CH₂Ph·COCl, AlCl₃, and α-C₁₀H₇·OMe in CS₂, gives o-4'-methoxy-1'-naphthoilmethylthiolbenzoic acid, m.p. 181—182°, cleaved by alkali to 4-methoxy-1-naphthyl α-hydroxybenzyl ketone, m.p. 162—163°, and (o-CO₂H·C₆H₄·S)₂. α-Naphthylbenzoin and SH·CH₂·CO₂H give (? impure) benzoinnaphthylbenzylthiolacetic acid, m.p. ~125° after softening, transformed by alkali into α-naphthyldeoxybenzoin, m.p. 106—107°, and H₂S but not BzOH. Non-cryst. α-benzoyl-β-phenylethylthiolacetic acid is cleaved to H₂S and CPh·CH₂·CH₂Ph, m.p. 70—71°. o-α-Benzoyl-β-phenylethylthiolbenzoic acid, m.p. 138—139°, is unchanged by protracted boiling with alkali. CPh·CH·CHPh and SH·CH₂·CO₂H melted together give β-benzoyl-α-phenylethylthiolacetic acid, m.p. 129—130° (rapidly yields CPh·CH·CHPh). o-Phenacylbenzylthiolbenzoic acid, m.p. 163°, from CPh·CH·CHPh and o-SH·C₆H₄·CO₂H or CPh·CH₂·CHPhCl and o-SH·C₆H₄·CO₂Na, is hydrolysed by cold, dil. Na₂CO₃ to CPh·CH·CHPh and o-SH·C₆H₄·CO₂H. m-Phenacylbenzylthiolbenzoic acid, m.p. 142°, is similarly cleaved to CPh·CH·CHPh and m-SH·C₆H₄·CO₂H. o-α-Benzoylstyrylthiolbenzoic acid, m.p. 174°, is hydrolysed by boiling 2N-NaOH to PhCHO and CH₂Bz·S·C₆H₄·CO₂H. CO(CH·CHPh)₂ and SH·CH₂·CO₂H give γ-keto-α-diphenyl-Δ⁵-pentenylthiolacetic acid, m.p. 126°, converted by 2N-NaOH into its components. Addition of PhMe to p-NO₂·C₆H₄·CH₂·COCl and AlCl₃ in CS₂ affords 4'-nitro-4-methyldeoxybenzoin, m.p. 114°, transformed by BzCl and NaOH in COMe₂ into the (impure) Bz derivative, m.p. 159—160°. H. W.

δδ-Dimethoxy-αδ-diphenylbutane-αγ-dione enol. R. E. LUTZ and J. M. SMITH, jun. (J. Amer. Chem. Soc., 1939, 61, 1465—1474).—The Ag salt of CPh·CH·C(OH)·COPh (I), when treated first with BzCl in boiling Pr⁶O, then with BzCl in MeOH, and subsequently hydrolysed by 10% NaOH-aq. MeOH, gives (on acidification with dil. HCl) γ-hydroxy-δδ-dimethoxy-αδ-diphenyl-Δ⁵-buten-α-one (II), m.p. 114° [red FeCl₃ colour; no reaction with o-C₆H₄(NH₂)₂], intermediates being OBz·CPh·CH·CO·COPh and OBz·CPh·CH·CO·CPh(OMe)₂ (III). A poorer yield

of (II) [with CPh·CH·C(OBz)·COPh (IV) and 3-keto-2-benzoyloxy-4-benzoyl-2:5-diphenyl-2:3-dihydrofuran] is obtained from the Na salt of (I); (I) itself reacts partly to give a little (IV) and, in one case, a trace of (II). Direct methylation of (I) to (II) could not be effected; the reverse change [(II) → (I)] is readily effected by hot HCl-AcOH, but (II) is stable to NaOH or NaOMe; a drop of H₂SO₄ in Ac₂O at 25° or MeOH-HCl at room temp. converts (II) into 3-keto-2-methoxy-2:5-diphenyl-2:3-dihydrofuran (V), thus proving the position of 1 OMe in (II). With O₃ in CHCl₃ at 0°, (II) reacts as if in equilibrium with OH·CPh·CH·CO·CPh(OMe)₂, yielding BzOH, MeOBz, and (presumably) (OMe)₂CPh·CO₂H (gives BzCO₂H on hydrolysis: identification as semicarbazone). With CH₂N₂ in Et₂O, (II) gives 52% of γδδ-trimethoxy-αδ-diphenyl-Δ⁵-buten-α-one (VI), m.p. 115°, and much oily αδδ-trimethoxy-αδ-diphenyl-Δ⁵-buten-γ-one (VII). The structure of (VI) is proved by conversion by HCl-MeOH into (V), hydrolysis by 25% NaOH-MeOH or HCl-AcOH to (II), and ozonolysis to BzOH and (OMe)₂CPh·CO₂Me, an oil (structure proved by hydrolysis). The structure of (VII) is shown by production of MeOBz by O₃ and by hydrolysis to (II). Me phenylglyoxylatesemicarbazone, m.p. 123.5°, is prepared for comparison from (a) NH₂·CO·NH·N·CPh·CO₂H, new m.p. 259° (decomp.), by CH₂N₂ and HCl-MeOH, (b) BzCO₂Me, and (c) CPh·CH·C(OMe)·COPh by O₃. The Na salt of (II) resists benzylation, but the Ag salt with BzCl in Pr⁶O gives impure (III) as an oil, the structure of which is assumed from ozonolysis to BzOH and MeOBz with only a trace of BzCO₂H, conversion by Ac₂O-H₂SO₄ or HCl-MeOH into (V), and hydrolysis to (II) by KOH in MeOH at 60°. The Na salt of (I) gives only traces of the α-OBz-compound, but the Ag salt with BzCl in Pr⁶O gives an oil, which is assumed (from its hydrolysis and ozonisation) to contain 60—70% of the α- and 20—30% of the γ-OBz-compound. Kurt Meyer titration of (II) indicates 92—94% enolisation. With Br in EtOH at -18°, (II) or its Na salt gives nearly 100% of β-bromo-δδ-dimethoxy-αδ-diphenyl-n-butane-αγ-dione, m.p. 122° (no FeCl₃ colour; stable to Br), reduced by KI, Na₂S₂O₄, or NaOEt to (II) and converted by Ac₂O-H₂SO₄ into the 4-Br-derivative of (V). The Ag salt of (II) and MeI in Pr⁶O give δδ-dimethoxy-αδ-diphenyl-β-methyl-n-butane-αγ-dione, m.p. 87° (no FeCl₃ colour), insol. in and fairly stable towards NaOH, stable to Na₂S₂O₄, and converted by HCl-MeOH or Ac₂O-H₂SO₄ into 3-keto-2-methoxy-2:5-diphenyl-4-methyl-2:3-dihydrofuran (VIII). The compound previously (A., 1938, II, 25) considered to be CPh·CMeBr·C(OMe)₂·COPh is probably 4-bromo-3-keto-2:5-dimethoxy-2:5-diphenyl-4-methyltetrahydrofuran, because it is stable to KI but is converted into (VIII) by Na₂S₂O₄ or H₂-Pd-CaCO₃. M.p. are corr. R. S. C.

Stereochemistry of halogenoimines. I. Determination of configuration of N-chloroket-imines by dipole moments. W. THEILACKER and K. FAUSER (Annalen, 1939, 539, 103—115).—The α-, m.p. 105°, and β-, m.p. 55°, -forms of p-chlorobenzophenonechloroimine (Peterson, A., 1911, i, 879) are anti- and syn-forms, respectively, since they

have dipole moments 2.47 ± 0.06 and 2.67 ± 0.05 (in these and other cases, $\times 10^{-18}$ e.s.u.), respectively. COPh_2 , $\text{CPh}_2\cdot\text{NCl}$ (I), and *benzophenonebromoisimine* (II), m.p. 38.5° , have dipole moments 2.99, 2.96 ± 0.04 , and 2.83 ± 0.03 , respectively. Individual bond moments are calc. (II) is obtained in 74% yield from $\text{CPh}_2\cdot\text{NH}\cdot\text{HCl}$ (best prepared at $120\text{--}140^\circ$; cf. Hantzsch *et al.*, A., 1892, 338), Br, Na_2CO_3 , and K_2CO_3 in H_2O at -3° . $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CPh}\cdot\text{NH}\cdot\text{HCl}$ gives similarly *p-chlorobenzophenonebromoisimine*, the two forms, m.p. 102° (unstable) and 73° , of which are probably stereoisomerides, although mixtures melt at 73° .

R. S. C.

Reaction of sodamide with fused aromatic ketones. L. C. FREIDLIN and T. F. BULANOVA (J. Gen. Chem. Russ., 1939, 9, 299—303).— NaNH_2 reacts with fused COPh_2 as follows: $\text{COPh}_2 + 2\text{NaNH}_2 \rightarrow \text{NaHCN}_2$ (I) + $\text{NaOH} + 2\text{C}_6\text{H}_6$. With other ketones the reactions are: $(\text{COPh})_2 + 4\text{NaNH}_2 \rightarrow 2(\text{I}) + 2\text{NaOH} + 2\text{C}_6\text{H}_6 + \text{H}_2$; fluorenone + $2\text{NaNH}_2 \rightarrow (\text{I}) + \text{NaOH} + \text{Ph}_2$; phenanthraquinone + $4\text{NaNH}_2 \rightarrow 2(\text{I}) + 2\text{NaOH} + \text{Ph}_2 + \text{H}_2$.

R. T.

Preparation of the hydrate of phenylglyoxal. R. BOUSSET (Bull. Soc. chim., 1939, [v], 6, 986—988).—Phenylglyoxal (I) [prep. from COPhMe (1 mol.) and SeO_2 (1 mol.) in boiling EtOH with fractionation] is converted by a limited amount of H_2O into the hydrate, m.p. 91° (from Et_2O); (I), liberated at $>100^\circ$, has b.p. $97^\circ/23$ mm.

A. T. P.

Action of organo-magnesium compounds on diacetyl- and benzil-dianil. M. MONTAGNE and M. GARRY (Compt. rend., 1939, 208, 1735—1737).— $(\cdot\text{CMe}\cdot\text{NPh})_2$ with MgMeI , MgEtBr (or I), and MgBu^tBr in warm Et_2O followed by alkaline hydrolysis affords *Me α -anilinoisopropyl ketone anil*, b.p. $155\text{--}157^\circ/3$ mm., m.p. $65\text{--}66^\circ$ (*picrate*, m.p. 150°), *Me α -anilino- α -methylpropyl ketone anil*, b.p. $218\text{--}219^\circ/20$ mm., m.p. $85\text{--}87^\circ$ [*picrate*, m.p. $113\text{--}114^\circ$ (? $143\text{--}144^\circ$) (decomp.)]; *Ac derivative*, m.p. 219° , and *Me α -anilino- α -methylamyl ketone anil*, m.p. 74° , respectively. Acid hydrolysis of the reaction products yields *Me α -anilinoisopropyl*, b.p. $153\text{--}155^\circ/24$ mm., m.p. 62° [*picrate*, m.p. $142\text{--}144^\circ$ (? $112\text{--}114^\circ$) (decomp.)]; *Ac derivative*, m.p. $73\text{--}74^\circ$; *oxime*, m.p. 141° , *Me α -anilino- α -methylpropyl*, b.p. $153\text{--}154^\circ/15$ mm., m.p. 45° [*picrate*, m.p. $94\text{--}95^\circ$; *oxime* (I), m.p. 82°], and *Me α -anilino- α -methylamyl ketone*, m.p. 84° [*picrate*, m.p. 130° (decomp.)]; *Ac derivative*, m.p. $71\text{--}74^\circ$; *oxime*, m.p. 96° , respectively. (I) is also obtained from MgEtI and β -oximino- γ -anilobutane. Similarly, MgMeI with $(\cdot\text{CPh}\cdot\text{NPh})_2$ affords *Ph α -anilino- α -phenylethyl ketone anil*, m.p. 154° (cf. A., 1937, II, 424), hydrolysed (HCl) to the ketone, (II), m.p. 142° . (II) does not react with MeI , Ac_2O , $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, or NH_2OH . With $\text{Zn}\text{--}\text{AcOH}$, (II) gives $\text{COPh}\cdot\text{CHPhMe}$ and NH_2Ph .

J. L. D.

cycloPropanone. N. J. DEMJANOV and V. V. FEOFILAKTOV (J. Gen. Chem. Russ., 1939, 9, 340—360).—Repetition of the work of Ingold *et al.* (J.C.S., 1921, 119, 305; 1922, 121, 1177) did not confirm production of cyclopropanone from cyclopropanol-1-mono- (I) or -1:2-di-carboxylic acid, nor could any substance yielding a cryst. semicarbazone be found

amongst the reaction products. In certain respects (ready oxidisability), (I) behaves rather as an olefine than as a cyclic compound; a comparison of its properties with those of the isomeric acids $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\text{CH}_3\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ (II), or $\text{EtCO}\cdot\text{CO}_2\text{H}$ shows that it is not identical with any of these, nor does it readily yield any of them by isomerisation. (I) and HBr at 100° yield an acid, $\text{C}_8\text{H}_{10}\text{O}_5$, m.p. $154\text{--}158^\circ$ (decomp.), identical with that obtained by van der Sleen from (II) (cf. A., 1901, i, 499). The chief product obtained from $(\text{CH}_3)_2\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ in EtOH and HCl is *Et β -chloro-ethylmalonate*, b.p. $145^\circ/24$ mm., instead of the expected $(\text{CH}_3)_2\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{Et}$.

R. T.

Supposed enolisation of cyclohexanone and other simple ketones. F. ARNDT and C. MARTIUS (Rev. Fac. Sci. Istanbul, 1939, 4, 88—90).—Pure cyclohexanone (I) does not at first decolorise acid-free Br in CCl_4 ; after 5—15 sec. the colour disappears, after which additional Br is immediately decolorised. Excess of EtOH or a trace of $\text{C}_6\text{H}_5\text{N}$ inhibits this decolorisation, but $\text{C}_6\text{H}_5\text{N}$ has no effect on the decolorisation of Br by $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$. (I) therefore contains no enol. The mechanism of this reaction and of the production of alkanes from (I) and metal alkyls (Grignard *et al.*, A., 1931, 465) and of RH from (I) and MgRX (cf. Kohler *et al.*, A., 1933, 1163) is discussed.

A. LI.

Oxidations catalysed by pervanadic acid. II. Oxidation and fission of saturated cyclic ketones. W. TREIBS (Ber., 1939, 72, [B], 1194—1199).—The main reaction is fission of the ring with production of aldehyde- or keto-acids. Only in the case of cyclohexanone (I) is oxidation somewhat resembling the biological type observed. The catalyst is obtained by covering V_2O_5 with 30% H_2O_2 whereby, after temporary dissolution, a brownish-yellow to green, voluminous product is obtained which dissolves in H_2O , alcohols, and COMe_2 in presence of H_2O_2 . Gradual addition of H_2O_2 to (I) and the catalyst in $\text{MeOH}\text{--}\text{H}_2\text{O}$ at room temp. gives cyclohexane-1:4-dione, m.p. $79\text{--}80^\circ$, adipic and *adipaldehydic acid*, b.p. $151\text{--}153^\circ/20$ mm. (*semicarbazone*, m.p. $159\text{--}160^\circ$). cycloPentanone yields glutaric and *glutaraldehydic acid*, b.p. $140\text{--}141^\circ/15$ mm. (*semicarbazone*, m.p. 159°). Menthone affords ϵ -keto- β -dimethyl-*n*-octoic acid, b.p. $170\text{--}175^\circ/15$ mm. (*semicarbazone*, m.p. 151°), whilst tetrahydrocarvone gives ϵ -keto- β -isopropylheptoic acid, b.p. $178\text{--}182^\circ/15$ mm. (*semicarbazone*, m.p. 150°), and a fraction, b.p. $140^\circ/15$ mm.

H. W.

Catalytic dehydrogenation using nickel. New applications. Kinetic experiments. L. PALFRAY, S. SABETAY, and A. HALASZ (Compt. rend., 1939, 208, 1654—1656).—Tetrahydroionol (I), b.p. $134.5^\circ/15$ mm., with 5% of used Ni (cf. A., 1939, II, 115) at $220^\circ/4$ hr. give tetrahydroionone (II) (78%); the yield is quant. if recovered (I) is re-treated. At $250^\circ/1$ hr., 80% of (II) is formed but a hydrocarbon appears as a by-product. Tetrahydromethylionol and β -decalol with Ni at 250° and 240° , respectively, give tetrahydromethylionone, b.p. $141\text{--}142^\circ/15$ mm., and β -decalone, b.p. $114\text{--}115^\circ/15$ mm. (*semicarbazone*, m.p. 197°), respectively. Repeated treatment

of cyclohexane-1 : 2-diol with Ni at 240°/2 hr. (ketone distilled after each operation) gives 2-ketocyclohexanol, m.p. 89° (tube), 135° (block). cycloHexane-1 : 3-diol (III) with Ni at 260° gives cyclohexanone (IV) quantitatively. cycloHexane-1 : 4-diol reacts slowly and gives 36% of the 1 : 4-diketone. The amount of (III) in a mixture of the three cyclohexanedols can be determined as (IV). Cholesterol similarly gives 70% of cholesterone in 1 hr. J. L. D.

Indones. XVI. Partial dehalogenation of the two 2 : 3-dichloro-3-phenyl-2-ethylhydrindones. R. DE FAZI and F. PIRONE (Gazzetta, 1939, 69, 166—171).—Further compounds are obtained by dehalogenation of the 2 : 3-dichloro-3-phenyl-2-ethylhydrindones, m.p. 94—96° (I) and 115—116° (II) (cf. A., 1937, II, 378). With Cu in EtOH at room temp., (I) gives a compound, C₁₇H₁₄OCl (*sic*), m.p. 145—146° (III); at the b.p., isomerides, m.p. 105—106° (IV) and 127—128° (V) (cf. *loc. cit.*) are formed. With AgNO₃ in EtOH at either temp., (I) gives (III); with KI at room temp. (III) and (IV) are formed; at the b.p. KI gives (IV). With EtOH-NH₃ at 0° or room temp., (I) gives (III). In boiling EtOH (II) with Cu gives (V); with KI, (IV). E. W. W.

γ-Ketonic acids. II. P. C. MITTER and L. K. DE (J. Indian Chem. Soc., 1939, 16, 199—208; cf. A., 1939, II, 267).—Methylsuccinic anhydride (I) with PhOMe in PhNO₂ containing anhyd. AlCl₃ at 0° affords only β-anisoyl-α-methylpropionic acid (II), m.p. 144° [semicarbazone, m.p. 162° (decomp.); Et ester (III), b.p. 185—187°/5 mm.], oxidised (HNO₃-AcOH at 100°/1 hr.) to p-OMe-C₆H₄-CO₂H, and with o-OH-C₆H₄-CHO in MeOH-dry HCl at 0° is converted into a pyrylium derivative, m.p. >300° (cf. Desai and Wali, A., 1938, II, 14). (III) (1 mol.) with MgMeI (1 mol.) in dry Et₂O gives Et γ-hydroxy-γ-p-anisyl-α-methylvalerate, b.p. 183—185°/6 mm., and the γ-lactone, b.p. 175—177°/5 mm., of γ-anisyl-α-methylvaleric acid, which is not reduced by Zn-boiling 10% NaOH. (II) when reduced (Clemmensen) gives γ-anisyl-α-methylbutyric acid, b.p. 180—182°/5 mm. (Et ester, b.p. 146—148°/4.5 mm.), converted by P₂O₅ in C₆H₆ at 100°/8 hr. into 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (IV), b.p. 150—152°/5 mm. (semicarbazone, m.p. 197°), reduced (Clemmensen) to 7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 114—115°/5 mm., dehydrogenated (Se at 310—320°/25 hr.) to 7-methoxy-2-methylnaphthalene, m.p. 89—90° (picrate, m.p. 119°). (IV) with MgMeI in dry Et₂O gives a mixture of carbinol and dehydrated product. (I) with PhOH in (CHCl₂)₂ containing anhyd. AlCl₃ at room temp. and then at 135—140°/6 hr. gives only β-salicyl-α-methylpropionic acid, m.p. 161° (Me ether, m.p. 92—94°; pyrylium derivative, m.p. >330°), reduced (Clemmensen) to γ-o-hydroxyphenyl-α-methylbutyric acid, b.p. 170—173°/5.5 mm., which is sulphonated but not cyclised by 85% H₂SO₄. m-C₆H₄(OMe)₂ with (I) in cold PhNO₂ containing AlCl₃ affords β-2 : 4-dimethoxybenzoyl-α-methylpropionic acid, m.p. 130—131° (pyrylium derivative, m.p. >280°), and a substance, m.p. 142—143°, separated by fractional crystallisation. Similarly, (I) and 1 : 2 : 3-C₆H₃(OMe)₃ afford a mixture of β-2-hydroxy-3 : 4-dimethoxy-

benzoyl-α-methylpropionic acid, m.p. 155° [pyrylium derivative; semicarbazone, m.p. 208—209°; Me ether, m.p. 89—90°; reduced (Clemmensen) to γ-2-hydroxy-3 : 4-dimethoxyphenyl-α-methylbutyric acid (V), m.p. 83—85°], and β-2-hydroxy-3 : 4-dimethoxybenzoyl-β-methylpropionic acid, m.p. 175—176°. (V) is cyclised by 85% H₂SO₄ at 100°/1.5 hr. to 5-hydroxy-1-keto-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 130—132° (semicarbazone, m.p. 228—229°), reduced (Clemmensen) to 5-hydroxy-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 152—154°/6 mm. J. L. D.

Benzanthrones. II. Synthesis of 1-alkylbenzanthrones-7. Mechanism of Bally's reaction. III. Synthesis of 2-alkyl- and -arylbenzanthrone-7. Migration [of methyl] from the 1- to the 2-position. F. G. BADDAR and F. L. WARREN (J.C.S., 1939, 944—948, 948—949; cf. A., 1938, II, 236).—αβ-Unsaturated aldehydes and ketones condense with anthrone according to Meerwein (A., 1919, i, 21), whereas CHPh:CH·CHO and aldehydes formed *in situ* from glycerols react as stated by Bally (cf. *loc. cit.*). (CH₂-CO₂)O, PhEt, and AlCl₃-PhNO₂-C₂H₅Cl₄ at -5°, then at 0° for 3 days, give β-p-ethylbenzoylpropionic acid, new m.p. 107—108°, reduced (Clemmensen) to γ-p-ethylphenylbutyric acid, new m.p. 74° [Et ester (I), b.p. 146—147°/8 mm.]. (I) and Et₂C₂O₄-KOEt-Et₂O afford Et α-oxalyl-γ-p-ethylphenylbutyrate (II), converted by 20% (vol.) H₂SO₄ into 7-ethyl-3 : 4-dihydro-1-naphthoic acid (III), m.p. 120°. Attempted hydrolysis of (II) with 15% (vol.) H₂SO₄ to α-keto-β-p-ethylphenylvaleric acid (not formed in this case), esterification, and then ring-closure by the method of Fieser *et al.* (A., 1938, II, 440) gives 7-ethyl-3 : 4-dihydronaphthalene-1 : 2-dicarboxylic acid, m.p. 165° [the anhydride, m.p. 117—118°, is also formed from (II)]; during the above hydrolysis, some β-p-ethylphenylethylmalonic acid, m.p. 145°, is formed. (III) and S at 200—210° (1 hr.) give 7-ethyl-1-naphthoic acid, m.p. 126°, oxidised by alkaline K₃Fe(CN)₆ to 1 : 7-C₁₀H₆(CO₂H)₂ (Me ester, m.p. 86°). Et γ-p-tolylbutyrate gives (as above) Et α-oxalyl-γ-p-tolylbutyrate, converted by 25—32% H₂SO₄ into 7-methyl-3 : 4-dihydro-1-naphthoic acid (IV), m.p. 153—154°, and some 7-methyl-3 : 4-dihydronaphthalene-1 : 2-dicarboxylic acid, m.p. 192°. (IV) gives 7 : 1-C₁₀H₆Me·CO₂H, the chloride of which with C₆H₅-AlCl₃-CS₂ gives Ph 7-methyl-1-naphthyl ketone (2 : 4-dinitrophenylhydrazones, α-, m.p. 256—257°, and β-form). Cyclisation with AlCl₃ gives no 1-methylbenzanthrone-7 (V); there is possible migration of Bz to afford 7 : 2- and 7 : 3-C₁₀H₆MeBz. Ph 7-ethyl-1-naphthyl ketone 2 : 4-dinitrophenylhydrazones, α-, m.p. 223—224°, and β-form, m.p. 200—210° (impure), and Ph α-C₁₀H₇ ketone 2 : 4-dinitrophenylhydrazones, α-, m.p. 246—247°, and β-form, m.p. 243—244°, are prepared similarly. 2 : 1-C₁₀H₆Me·NH₂ affords 1-iodo-2-methylnaphthalene, b.p. 155°/3 mm., which with o-C₆H₄I·CO₂Me and Cu-bronze at 180—190° gives o-2'-methyl-1'-naphthylbenzoic acid, m.p. 188—189°, which, through the chloride (Friedel-Crafts), gives (V) (cf. *loc. cit.*), identical with the product from CHMe:CH·CHO, anthrone, and H₂SO₄.

CHPh:CH·COMe, anthrone, and MeOH (+ piperidine) at 100° (bath) give β -phenyl- β -anthronylethyl Me ketone, m.p. 116—117°, converted by 80% H_2SO_4 -AcOH- As_2O_5 at 100° (bath) into 1-phenyl-3-methylbenzanthrone-7, m.p. 176°. Condensation of α -ethylglycerol and anthrone in presence of H_2SO_4 yields 3- but no 1-ethylbenzanthrone-7. 2:1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{NHAc}$ has new m.p. 200°.

III. β -Methylglycerol $\alpha\gamma$ - Et_2 ether, b.p. 175°, and anthrone (method: A., 1938, II, 236) (purification by distilling with superheated steam at 200°) afford 2-methylbenzanthrone-7 (VI), m.p. 165—166°. Similarly prepared are the 2-Ph, m.p. 200°, and 2-Et analogue, m.p. 117°. (V) and AlCl_3 -NaCl at 150° give (VI) by migration of Me. A. T. P.

Attempted syntheses of natural sterols. III. Syntheses of tetracyclic ketones. G. HABERLAND.

IV. Extension of the Reformatsky synthesis. G. HABERLAND and E. HEINRICH (Ber., 1939, 72, [B], 1215—1221, 1222—1226; cf. A., 1937, II, 104).—III. γ -6-Methoxy-1-naphthyl- β -methyl- n -butyric acid (I) is converted by POCl_3 in C_6H_6 into the chloride, which condenses with $\text{CHNa}(\text{CO}_2\text{Et})$ in C_6H_6 ; the product is hydrolysed to ϵ -6-methoxy-1-naphthyl- γ -methylpentan- β -one, identified as the 2:4-dinitrophenylhydrazone, m.p. 172°. (I) is converted by the successive action of SOCl_2 , CH_3N_2 , and 48% HBr into α -bromo- ϵ -6-methoxy-1-naphthyl- γ -methylpentan- β -one (2:4-dinitrophenylhydrazone, m.p. 165—166°), transformed by condensation with $\text{CHNa}(\text{CO}_2\text{Et})_2$ followed by hydrolysis and esterification with CH_3N_2 into Me γ -keto- ζ -6-methoxy-1-naphthyl- δ -methyl- n -heptoate, b.p. 170—175°/0.05 mm. [free acid (II), m.p. 92—93°]. γ -Keto- ζ -6-methoxy-1-naphthyl- n -heptoic acid has m.p. 88°. (II) is converted by conc. H_2SO_4 at 0° into the lactone (A), m.p. 198°, of β -2-hydroxy-7-methoxy-2-methyl-1:2:3:4-tetrahydro-1-phenanthrylpropionic acid; the acid, m.p. 163°, is converted by warm, dil. HCl into a lactone (III), m.p. 230°. Treatment of (II) with CH_3N_2 and then with conc. H_2SO_4 -AcOH affords Me β -7-methoxy-2-methyl-3:4-dihydro-1-phenanthrylpropionate (IV), b.p. 160—170°/0.04 mm., m.p. 137°, hydrolysed by KOH-MeOH to (III). Hydrolysis of (IV) [or (A)] with $\text{Ba}(\text{OH})_2$ and treatment of the Ba salt with PCl_5 yields the acid chloride, converted by SnCl_4 at -20° into the tetracyclic ketone, $\text{C}_{19}\text{H}_{18}\text{O}_2$, m.p. 205—207°; if the mixture is boiled after addition of SnCl_4 a ketone, $\text{C}_{19}\text{H}_{16}\text{O}_2$, m.p. 170°, is obtained.

IV. $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ may be used in place of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$. Reaction generally starts less readily and proceeds less vigorously so that it is advisable to use the finely divided metal and a solvent of higher b.p. such as PhMe. 1-Keto-6-methoxy-1:2:3:4-tetrahydronaphthalene, Mg powder, and $\text{CH}_2\text{Br}(\text{Cl})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ give the OH-ester, converted by hydrolysis and distillation (b.p. 185—190°/0.3 mm.) into β -6-methoxy-3:4-dihydro-1-naphthylpropionic acid (I), m.p. 117.5—118°. β -6-Methoxy-1:2:3:4-tetrahydronaphthylethyl bromide and NaCN in COMe_2 yield the corresponding nitrile, hydrolysed to β -6-methoxy-1:2:3:4-tetrahydro-1-naphthyl propionic acid, m.p. 77°, dehydrogenated (S at 220—240°) to β -6-methoxy-1-naphthylpropionic acid, also

obtained by dehydrogenation of (I). P_2O_5 in boiling C_6H_6 converts (I) into 1'-keto-6-methoxy-3:4-dihydro-3':2':1:2-cyclopentenonaphthalene (semicarbazone, m.p. 248°). 1-Keto-7-methoxy-2-methyl-1:2:3:4-tetrahydrophenanthrene, Mg powder, and $\text{Br}[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ in boiling PhMe afford β -1-hydroxy-7-methoxy-2-methyl-1:2:3:4-tetrahydro-1-phenanthrylpropionolactone, m.p. 194°, converted by successive treatments with $\text{Ba}(\text{OH})_2$, PCl_5 , and SnCl_4 into the above ketone, $\text{C}_{19}\text{H}_{16}\text{O}_2$, m.p. 170°. H. W.

Degradation of stigmasterol to allopregnan-20-one. L. MAMOLI (Gazzetta, 1939, 69, 240—245).—Stigmasterol is converted (method: Fernholz, A., 1933, 1290) into Me bisnorallocholanate, which with Mg and PhBr in Et_2O gives 20-diphenylmethyleneallopregnane, m.p. 170°, oxidised in CHCl_3 by O_3 to allopregnan-20-one, m.p. 134°. E. W. W.

Hormones related to sterols. I. 7-Keto- Δ^5 -androstene-3:17-diol diacetate. A. OGATA and I. KAWAKAMI (J. Pharm. Soc. Japan, 1938, 58, 18—23).— Δ^5 -Androstene-3:17-diol diacetate, m.p. 165—166°, obtained by reducing dehydroandrostene with Na and boiling Pr^+OH and acetylating the product, is oxidised by CrO_3 in AcOH to 7-keto- Δ^5 -androstene-3:17-diol diacetate, m.p. 217—218° (oxime, m.p. 226°, complete decomp. 235°). H. W.

Absorption spectra of the compounds formed by androsterone and testosterone in the m -dinitrobenzene reaction. G. O. LANGSTROTH and N. B. TALBOT (J. Biol. Chem., 1939, 128, 759—774).—The absorption spectra of the compounds from androsterone (I) and testosterone (II) with m - $\text{C}_6\text{H}_4(\text{NO}_2)_2$ (III) in EtOH-KOH are measured between 2800 and 7000 Å.; (I) and (II) give different spectra, and the differences permit fairly accurate determinations of the amounts of (I) and (II) in EtOH solutions of mixtures of both. There is evidence that the reaction between (I) and (III) is influenced by the presence of (II), and in very accurate determinations this factor must be considered. Results of spectrochemical analysis of known synthetic mixtures of (I) and (II) are in good agreement with results of biological assays. J. D. R.

Bacterial oxidation of methylandrostenediol to methyltestosterone. L. MAMOLI (Gazzetta, 1939, 69, 237—240).—Methylandrostenediol in sterile yeast buffered with $\text{NaHPO}_4\cdot\text{KH}_2\text{PO}_4$ and treated at 32° with dehydrogenating bacteria (cf. A., 1938, II, 414) gives 75% of methyltestosterone. E. W. W.

Sterols. XIII. Esters of methyltestosterone. S. KUWADA and M. MIYASAKA (J. Pharm. Soc. Japan, 1939, 58, 59—60).—17-Methyl- Δ^5 - β -trans-androstene-3:17-diol (I) with Ac_2O [AcCl or $\text{Ac}_2\text{O}-\text{C}_2\text{H}_5\text{N}$ gives oily material or unchanged (I)] affords the diacetate, m.p. 146°, hydrolysed (MeOH-KOH) to the 17-monoacetate, m.p. 164°, which when treated successively with Br, CrO_3 -AcOH, and Zn dust yields 17-methyltestosterone acetate, m.p. 177° (semicarbazone, decomp. 238°). The dipropionate, m.p. 83° [prep. with $(\text{EtCO})_2\text{O}$], of (I) is similarly converted into the monopropionate, m.p. 138°, and thence into 17-methyltestosterone propionate, m.p. 146° (semicarbazone, decomp. 230°). M.p. are corr. Various

attempts to acetylate methyltestosterone were unsuccessful.

H. B.

Oestrone sulphate, a physiological excretion product of follicle hormone. A. BUTENANDT and H. HOFSTETTER (Z. physiol. Chem., 1939, 259, 222—234).—Oestrone and ClSO_3H in anhyd. $\text{C}_5\text{H}_5\text{N} + \text{CHCl}_3$ at 20° for 24 hr. give oestrone sulphate [$\text{Na} (+\text{H}_2\text{O})$ (I), m.p. 228—230° (corr.), $[\alpha]_D^{25} +110^\circ$ (semicarbazone, decomp. 258—260°), $\text{C}_5\text{H}_5\text{N}$, m.p. 173—175°, $[\alpha]_D^{25} +84.1^\circ$, quinine, m.p. 168—170°, and quinidine ($+3\text{H}_2\text{O}$) salt (II), m.p. 167—170°]. Oestrone and ClSO_3H in boiling $\text{CHCl}_3\text{--CCl}_4\text{--Et}_2\text{O}$ (little) afford *oestronesulphonic acid* (III), m.p. 210° [Me_2 derivative (IV) (CH_2N_2), sinters 197° , then solidifies with m.p. 207°]. (I) is very easily decomposed, and in presence of phenolsulphatase 90% is hydrolysed after 16 hr. at 37° . The absorption curve in the ultra-violet is similar to that of oestrone acetate. The physiological activity of (I) is not comparable with that of oestrone for esterification of the OH greatly reduces the oestrogenic action; 10 $\mu\text{g.}$ is active in the Allan-Doisy test on castrated mice. The same result is obtained by injection (in oil or Ringer's solution) or oral administration. (II) shows the same activity as (I) when injected subcutaneously in oil. 1 $\mu\text{g.}$ of the $\text{C}_5\text{H}_5\text{N}$ salt is active when injected in oil, but twice and three times this amount are needed when injected subcutaneously in Ringer's solution and administered orally respectively. (III) and (IV) are inactive. Isolation of crude oestrone sulphate from pregnancy urine and urine of pregnant mares confirms the results of Schachter and Marrian (A., 1937, III, 150; 1939, III, 264). J. N. A.

Sterols. LXV. Progesterone from allo-pregnane-3-dione. R. E. MARKER, E. L. WITTE, and L. PLAMBECK, jun. (J. Amer. Chem. Soc., 1939, 61, 1333—1335).—2-Bromoallopregnane-3:20-dione and $\text{C}_5\text{H}_5\text{N}$ give the *pyridinium bromide*, $\text{C}_{26}\text{H}_{36}\text{O}_2\text{NBr}$, m.p. 300—302° (decomp.), which, when heated at 10 mm. and then distilled in a "mol." still, yields ~ equal amounts of progesterone and $\Delta^{1:2}$ -allopregnene-3:20-dione (I), m.p. 208—210° (dioxime, m.p. 248—250°). Hydrogenation of (I) gives, according to the conditions, *allopregnane-3(β):20(β)-diol* or *allopregnan-3(β)-ol-20-one* (oxidised to the known dione). NaOMe-MeOH or KOH-MeOH equilibrates *allopregnane-3:20-dione* with *isoallopregnane-3:20-dione*, new m.p. 148—149°, the difference in structure being at C_{17} . R. S. C.

Sterols. XV. Synthesis of Δ^4 -bisorcholestone-3:24-dione. S. KUWADA and S. YOSIKI (J. Pharm. Soc. Japan, 1938, 58, 187—189).— Δ^5 -Acetylcholeonic acid is converted by the successive action of SOCl_2 and $\text{Et}_2\text{O-CH}_2\text{N}_2$ into the corresponding diazoketone, $\text{C}_{27}\text{H}_{40}\text{O}_3\text{N}_2$, decomp. 153° , which with HCl in EtOH or CHCl_3 affords 25-chloro-3-acetoxy- Δ^5 -bisorcholesten-24-one, m.p. 187° . Reduction (Zn powder, AcOH) and subsequent hydrolysis (MeOH-KOH) of this gives 3-hydroxy- Δ^5 -bisorcholesten-24-one, m.p. 116—129° [semicarbazone ($+ \text{H}_2\text{O}$), decomp. 194° ; oxime, decomp. 173—179°; acetate, m.p. 145—151° (semicarbazone, decomp. 211° ; oxime, m.p. 152—155°)], oxidised by Al(OPh)_3 in C_6H_6 to Δ^4 -bisorcholestone-3:24-dione, m.p. 152°

(dioxime, decomp. 117° ; 3-mono-, decomp. 217° , and di-semicarbazone, decomp. 234°). H. B.

Oxidation of *p*-cresol by means of tyrosinase. C. A. BORDNER and J. M. NELSON (J. Amer. Chem. Soc., 1939, 61, 1507—1513).—It is shown that *o*-benzoquinone does not spontaneously oxidise PhOH or *p*-cresol (I) to the *o*-dihydric phenols and that tyrosinase does not catalyse oxidation of (I) to 4:1:2- $\text{C}_6\text{H}_3\text{Me(OH)}_2$ (II) by H_2O_2 or 4-methyl-*o*-benzoquinone (III). The induction period for aerobic oxidation of (I) by tyrosinase is shortened by increasing the alkalinity or adding reducing agents [$\text{K}_4\text{Fe(CN)}_6$, alanine, quinol, or H_2O_2], and lengthened by adding PhSO_2Na or agents capable of oxidising (II) to (III) [$\text{K}_3\text{Fe(CN)}_6$, MnO_2 , or laccase]. It is concluded that tyrosinase is unable to act on a monohydric phenol until it has first effected oxidation of an *o*-dihydric phenol. Oxidation of (I) then occurs by the reaction, $(\text{I}) + (\text{II}) + \text{O}_2 \rightarrow (\text{III}) + (\text{II}) + \text{H}_2\text{O}$. Autocatalysis of the reaction is due to the amount of (II) increasing by virtue of the reaction, $2(\text{III}) + \text{H}_2\text{O} \rightarrow (\text{II}) + 5\text{-hydroxy-4-methyl-}o\text{-benzoquinone}$. R. S. C.

N-Substituted amino-*p*-quinones. S. KANAO and S. INAGAWA (J. Pharm. Soc. Japan, 1938, 58, 71—76).—In Et_2O or CHCl_3 , *p*-benzoquinone gives the following products: with Et_2 *l*-aspartate, *Et*₄ *benzoquinonebis(aminosuccinate)*, m.p. 97° ; with Et_2 *d*-glutamate, *Et*₄ *benzoquinonebis(α-aminoglutarate)*, m.p. 83° ; with $\text{NH}_2\text{[CH}_2\text{]}_2\text{OH}$, *bis(β-hydroxyethylamino)-*, m.p. 262° ; with *iso*- $\text{C}_5\text{H}_{11}\text{NH}_2$, *isomethylamino-*, m.p. 169° ; with $\text{CH}_2\text{Ph-CH}_2\text{NH}_2$, *mono-*, m.p. 147—150° or *bis(β-phenylethylamino)-*, m.p. 222—223°; with $\text{OH-CHPh-CH}_2\text{NH}_2$, *bis(β-hydroxy-β-phenylethylamino)-*, m.p. 273° ; with tyramine, *bis(β-p-hydroxyphenylethylamino)-*, m.p. 237—238° [converted by Pt-H_2 and dil. HCl into the quinol *dihydrochloride*, m.p. ~ 237° (decomp.)]; with cadaverine, *ε-aminoamylamino-*, m.p. ~130—160° (sinters 120°), and with histamine, *bis(β-4-glyoxalinyethylamino)-benzoquinone*, m.p. 257° . E. W. W.

Preparation and m.p. of 1-iodoanthraquinone. A. E. GOLDSTEIN (J. Amer. Chem. Soc., 1939, 61, 1600—1601).—1-Iodoanthraquinone, m.p. 204—205° (corr.) (lit., 177° , 176°), is obtained in 90% yield from the amine. Laubé's procedure (A., 1907, i, 941) gives a poor yield. R. S. C.

Anthraquinone group. II. Phthaloylation. G. B. CRIPPA and R. CARACCI (Gazzetta, 1939, 69, 268—275).—1-Amino-2-methylanthraquinone (I) and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ (II) at 235° for 5 hr. give $\text{NN'-bis(2-methyl-1-anthraquinonyl)phthalamide}$ (III), m.p. 221—222°, hydrolysed (5% NaOH) to (I) and the *Na* salt of *N*-2-methyl-1-anthraquinonylphthalamic acid (IV). With boiling Ac_2O (III) yields 1-*phthalimido*-2-methylanthraquinone (V), m.p. 261° , and the *Ac* derivative of (I). The *Ac* derivative is also formed from (I) and (II) in boiling Ac_2O ; this reaction, and the failure to obtain (V) direct from (I), are ascribed to an enol-imine tautomerism of both (I) and (III). With cone. H_2SO_4 at 100° , (V) gives (I). Attempts to eliminate H_2O from (V) by heating at 280° or boiling with P_2O_5 in PhNO_2 were unsuccessful; with KOH at 185° (V)

gives the *K* salt of (IV). 1-Amino-2-anilomethyl-anthraquinone with (II) at 240° gives 1-*phthalimido*-2-anilomethylanthraquinone (VI), m.p. 315°, and 1-*phthalimidoanthraquinone*-2-aldehyde, m.p. 338°, converted into (VI) by heating with NH_2Ph . E. W. W.

Linear hexacene series. C. MARSCHALK (Bull. Soc. chim., 1939, [v], 6, 1112—1121; cf. A., 1938, II, 236).—2 : 3- $\text{C}_{10}\text{H}_8(\text{CO})_2\text{O}$ and 2 : 3-dihydroquinizarin with a little AlCl_3 at 285—290° give 5 : 7 : 14 : 16-tetrahydroxyhexacene-6 : 15-quinone (I) (probably formed through an isomeride). 1 : 4-Dihydroxy-6 : 7-benzanthraquinone (II) and $\text{Na}_2\text{S}_2\text{O}_4$ in aq. $\text{C}_5\text{H}_5\text{N}$ give the 2 : 3- H_2 -derivative, converted by $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O-AlCl}_3$ at 270° into (I). (II) and $o\text{-CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ in aq. alkaline $\text{Na}_2\text{S}_2\text{O}_4$ afford 1 : 4-dihydroxy-2-*o*-carboxybenzyl-6 : 7-benzanthraquinone, cyclised by $\text{AlCl}_3\text{-NaCl}$ at 150—160° to (?) 6 : 15-dihydroxy-5 : 7 : 14-triketo-5 : 7 : 14 : 16-tetrahydrohexacene, which is oxidised by $\text{Mn}_2(\text{SO}_4)_3$ to 7 : 14-dihydroxyhexacene-5 : 16-6 : 15-diquinone [can be reduced ($\text{Na}_2\text{S}_2\text{O}_4$; $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O-PhNO}_2$) to (I)], also obtained by air oxidation of (I) in aq. alkali. (I) is reduced by H_2 in presence of Zn at 300° to 5 : 16-dihydro-*lin*-hexacene, m.p. 369—370° (block), dehydrogenated (Pd-C in $\text{C}_6\text{H}_3\text{Cl}_3$ and CO_2 at ~195°) to *lin*-hexacene. A. T. P.

Menthone series. XV. *l*-trans- Δ^4 -menthen-3-ol. D. MALCOLM and J. READ (J.C.S., 1939, 1037—1040).—Reduction (Ponndorf) of *l*- Δ^4 -menthen-3-one yields *l*-trans- (I), b.p. 102—104°/18 mm., $[\alpha]_D^{25}$ —165.7° in EtOH (*p*-nitrobenzoate, m.p. 55°, $[\alpha]_D^{25}$ —210.0° in CHCl_3), and *l*-cis- Δ^4 -menthen-3-ol (II) (obtained impure), separated by their 3 : 5-dinitrobenzoates, the former (less sol.), m.p. 164—165°, $[\alpha]_D^{25}$ —175.0° in CHCl_3 . The menthenols conform to the Auwers-Skita rule. (I) is partly racemised by heating with HCl, reacts more readily than (II) with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$, and is reduced (Pd-gum arabic) to *d*-isomenthol (with some *trans-p*-menthane), whilst (II) on reduction gives *l*-menthol, *l*-menthone, and *trans-p*-menthane. Thus it is possible to convert *l*-nienthol into *d*-isomenthol (cf. Grubb and Read, A., 1934, 413). Reduction (Ponndorf) of *dl*- Δ^3 -menthen-3-one (from *dl*- Δ^3 -menthene via the nitroschloride and oxime) yields *dl*- Δ^4 -menthen-3-ol, b.p. 113—117°/35 mm. (3 : 5-dinitrobenzoate, m.p. 135°). A. Li.

Cineolecarboxylic acids. A. GANDINI (Gazzetta, 1939, 69, 177—190).—2-Chloro- with NaI in COMe_2 gives 2-iodo-cineole, b.p. 60—62°/0.15 mm., which with AgCN in EtOH at 140° forms 2-cyano-cineole, b.p. 78—80°/0.2 mm.; this boiled (20 hr.) with 10% KOH-MeOH gives cineole-2-carboxylic acid, b.p. 98—101°/0.2 mm. (*Ag* salt). The pernitrosoderivative of ketocineole (I) in EtOH with aq. KCN gives a *K* salt, $\text{C}_{11}\text{H}_{19}\text{O}_3\text{N}_3\text{K}$ (*Ag* analogue), which when acidified and heated at 80—90° gives 2-hydroxy-cineole-2-carboxylamide (III), m.p. 208—209°, oxidised by 5% KMnO_4 to cineolic acid, or by PbO_2 to (I). 10% EtOH-KOH, or EtOH-HCl, does not hydrolyse (III), but with boiling aq. HCl this gives cymene-2-carboxylic acid and *dl*-carvone, with cymene-2-carboxylamide, new m.p. 144—145°. With 20% H_2SO_4 followed by NaNO_2 , (III) gives a very small yield of 2-hydroxycineole-2-carboxylic acid, m.p. 135° (sublimes

90°/0.2 mm.). By Na in EtOH, (III) is reduced to menthane-2-carboxylamide, m.p. 183° (sublimes 113—115°/0.01 mm.) (oxidised to *dl*-tetrahydrocarvone), with some cineole-2-carboxylamide (?), m.p. 160—162° (sublimes 103—105°/0.01 mm.), and oily products. With HCl in dry Et_2O , (II) gives 2-chlorocineole-2-carboxylamide, m.p. 139°, which with NH_2Ph forms two forms (?), m.p. 130° and 127°, of 2-anilinocineole-2-carboxylamide. With $\text{NH}_3\text{-EtOH}$, two substances are obtained, regarded as 2-aminocineole-2-carboxylic acid, m.p. 121—122°, and the corresponding internal amide, m.p. 105—106°. E. W. W.

Action of organo-magnesium derivatives on pulegone. J. DŒUVRE (Bull. Soc. chim., 1939, [v], 6, 1067—1069).—Pulegone and $\text{CH}_2\text{Bu}^t\text{MgBr}$ give isoamylmenthane, $\text{CHMe}\langle\text{CH}_2\text{-CO}\rangle\text{CH}\cdot\text{CMe}_2\cdot\text{C}_5\text{H}_{11}$ (3 parts), b.p. 110°/2 mm., $[\alpha]_D^{20}$ —8.97° (oxime, b.p. 123—125°/1 mm.) (purified through the semicarbazone), and isoamylpulegol, $\text{CHMe}\langle\text{CH}_2\text{-C(OH)(C}_5\text{H}_{11})\rangle\text{C}\cdot\text{CMe}_2$ (2 parts), b.p. 107—109°/2 mm. A. T. P.

Addition of maleic anhydride to terpene hydrocarbons. K. HULTZSCH (Ber., 1939, 72, [B], 1173—1187; cf. B., 1939, 293).—Terpene hydrocarbons with isolated double linkings, when boiled for several hr. with maleic anhydride (I), yield 1 : 1 adducts from which dibasic acids having the following m.p. have been prepared: *d*- and *l*- α -pinene (II) 169°, *d*- and *l*-limonene (III) 147°, terpinolene 182° [*Me* ester 110°], Δ^3 -(? or Δ^4 -)carene (IV) 183°. (II) and (IV) also give smaller quantities of a substance identical with the α -phellandrene-(I) adduct (A., 1928, 1018). The hydrocarbons named in (II)–(IV) react rapidly and exothermally with maleic acid, undergoing mol. rearrangement to form the α -terpinene adduct anhydride (A., 1938, II, 330). None of the above is identical with the *alloocimene*-(I) adduct (V). (V) with ZnCl_2 and AcOH gives an isomeric anhydride, m.p. 227°. The acid (VI) corresponding with (V) is converted by boiling Ac_2O into an isomeric acid (VII), m.p. 189°, whilst the Me_2 ester of (V) or (VI) affords (boiling NaOMe-MeOH) a second isomeric acid, m.p. 226°. Boiling dil. H_2SO_4 converts (VI) into a dilactone, m.p. 186°, partial hydrolysis of which gives a monolactonic acid, m.p. 243°. (II)–(IV) are regarded as terpenylsuccinic anhydrides formed by H migration, on the grounds of their non-identity with (V), failure of their Me_2 esters to afford *trans*-acids, and retention of optical activity in (II), (III), and (IV). F. L. U.

Passerini's reaction [of camphor and terpenes]. A. GANDINI (Gazzetta, 1939, 69, 190—194).—The *K* salt from pernitrosocamphor and KCN gives, with HCl in dry Et_2O , the compound $\text{C}_{11}\text{H}_{17}\text{ON}$ (I) obtained by Passerini (A., 1925, i, 1290) from the salt and H_2SO_4 , and regarded by him as camphorecyanohydrin, and by Houben *et al.* (A., 1931, 358) as camphenecarboxylamide. With conc. HCl, (I) gives Houben's 2-chloro-camphane-2-carboxylamide (A., 1926, 731); this is reduced by Pt-H_2 to a substance, $\text{C}_{22}\text{H}_{35}\text{O}_2\text{N}_2\text{Cl}$, m.p. 151—152° (sublimes 110—112°/0.01 mm.). E. W. W.

cyclo-Dehydration of certain substituted camphenilanols. B. A. ARBUSOV (J. Gen. Chem. Russ.,

1939, 9, 239—248).—Camphenilanealdehyde (I) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ in Et_2O yield *benzylcamphenilanylcarbinol*, b.p. 183—185°/5 mm., m.p. 71—72°, which with 90% H_2SO_4 at $\geq 20^\circ$ affords 1:1-dimethyl-2:12-endomethyleno-1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 132.5—133.5°/1 mm. *Phenylcamphenilanylcarbinol*, b.p. 153—155°/3 mm., m.p. 80—81°, similarly yields a *hydrocarbon*, $\text{C}_{10}\text{H}_{20}$, b.p. 110.5—111°/0.3 mm., which may be 1:1-dimethyl-2:11-endomethyleno-1:2:3:4:10:11-hexahydrofluorene, or 9:9-dimethyl-1:6-endomethyleno- or 6:6-dimethyl-7:9-endomethyleno-2:3-benzo-1:3:3-dicyclo- Δ^2 -nonene. (I) and $1\text{-C}_{10}\text{H}_7\cdot\text{MgCl}$ afford unstable β -naphthylcamphenilanylcarbinol, which splits off H_2O during distillation, yielding 2- α -naphthylidene-1:1-dimethyl-3:6-endomethylenocyclohexane, b.p. 185.6—188°/1 mm. (*picrate*, m.p. 111—112°); this undergoes condensation in presence of H_2SO_4 , giving a *hydrocarbon*, $\text{C}_{10}\text{H}_{22}$, b.p. 185—186°/1 mm., probably 8:8-dimethyl-9:12-endomethyleno-7:8:9:10:11:12:13-heptahydrobenzanthrene. The product of condensation of campholenaldehyde and $1\text{-C}_{10}\text{H}_7\cdot\text{MgCl}$ reacts with H_2SO_4 yielding a *hydrocarbon*, $\text{C}_{10}\text{H}_{22}$, b.p. 165—167°/0.5 mm., probably a cholane derivative.

R. T.

Isomerisation of terpene oxides. II. Isomerisation of α -pinene oxide in the Grignard reaction. III. Isomerisation of camphene, nopinene, and Δ^3 -carene oxides in the Reformatski reaction. B. A. ARBUOV (J. Gen. Chem. Russ., 1939, 9, 249—254, 255—271).—II. The results of Ritter and Russell (A., 1936, 475) are confirmed. *l*- α -Pinene oxide (I) or campholenaldehyde and MgPhBr in Et_2O yield phenylcampholenol, oxidised (CrO_3 in AcOH) to *phenylcampholenone*, b.p. 138—140°/1.5 mm. (*semicarbazone*, m.p. 162—163°). (I) does not react with ZnEt_2 in C_6H_6 at the b.p.; in absence of solvent, and at 160°, an *alcohol*, $\text{C}_{12}\text{H}_{24}\cdot\text{OH}$, b.p. 81.5—82.5°/2.5 mm., $[\alpha]_D^{20} -10.94^\circ$, is obtained. The pinane structure is postulated for this alcohol.

III. Camphene oxide, distilled from ZnBr_2 , yields camphenilanealdehyde and isocamphenilanic acid, whilst with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (II) and Zn the product is *Et* β -hydroxy- β -(2:2-dimethyl-1:2:2-dicyclo-3-heptyl)propionate, b.p. 131.5—132.5°/3 mm., from which the corresponding *acid*, m.p. 111—112°, is obtained by hydrolysis. Nopinene oxide similarly gives dihydromyrtanal with ZnCl_2 or ZnBr_2 , and *Et* β -hydroxy- β -(7:7-dimethyl-1:1:3-dicyclo-2-heptyl)propionate, b.p. 137—138.5°/2.5 mm., with (II) and Zn . Δ^3 -Carene oxide, b.p. 80—80.5°/13 mm., $[\alpha]_D^{20} +11.25^\circ$, and ZnBr_2 yield an unsaturated *aldehyde*, $\text{C}_{10}\text{H}_{16}\text{O}$, b.p. 69—69.5°/3 mm., $[\alpha]_D^{20} +9.57^\circ$, of undetermined structure, together with *p*-cymene. An *ester*, $\text{C}_{14}\text{H}_{24}\text{O}_3$, b.p. 136—137°, containing one double linking, is obtained with (II) and Zn , and yields an unsaturated *acid*, $\text{C}_{11}\text{H}_{17}(\text{OH})\cdot\text{CO}_2\text{H}$, m.p. 125°, when hydrolysed.

R. T.

Thujone series. II. Catalytic hydrogenation of *d*-sabinol. A. G. SHORT and J. READ (J.C.S., 1939, 1040—1045; cf. A., 1939, II, 79).—Hydrogenation (PtO_2) of *d*-sabinol, b.p. 90°/11 mm., $[\alpha]_D^{20} +3.94^\circ$ (homogeneous) (*p*-nitrobenzoate, $[\alpha]_D^{20} +10.0^\circ$ in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 109°, $[\alpha]_D^{20} +22.5^\circ$

in CHCl_3 ; acetate, b.p. 101—102°/11.5 mm., $[\alpha]_D^{20} +79.9^\circ$ in CHCl_3 ; *H* phthalate, m.p. 101—102°, $[\alpha]_D^{20} -17.5^\circ$ in MeOH ; propionate, $[\alpha]_D^{20} +61.8^\circ$ in CHCl_3 ; *n*-butyrate, $[\alpha]_D^{20} +48.3^\circ$ in CHCl_3 ; benzoate, $[\alpha]_D^{20} +20.0^\circ$ in CHCl_3 ; cinnamate, $[\alpha]_D^{20} +9.8^\circ$ in MeOH), yields a mixture of alcohols, chiefly *l*-neothujyl alcohol, m.p. 22—23°, $[\alpha]_D^{20} -7.54^\circ$ in PhMe (cf. "tanacetyl alcohol," Tschugaev *et al.*, A., 1912, i, 479) (*p*-nitrobenzoate, m.p. 90°, $[\alpha]_D^{20} -12.5^\circ$ in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 103°, $[\alpha]_D^{20} -10.0^\circ$ in CHCl_3), oxidised (CrO_3) to *l*-thujone. Partial reduction (Pd sol) of *d*-sabinyl acetate yields *d*-2:3-dimethyl-4-isopropyl- Δ^2 -cyclopentenol (I), b.p. 90—91°/10 mm., $\alpha_D^{15} +28.22^\circ$ (*l* 1, homogeneous) (*p*-nitrobenzoate, m.p. 46.5°, $[\alpha]_D^{15} +93.5^\circ$ in CHCl_3 ; 3:5-dinitrobenzoate, m.p. 63—64°, $[\alpha]_D^{20} +64.75^\circ$ in CHCl_3), oxidised (CrO_3) to the ketone, b.p. 89°/13 mm., $\alpha_D^{15} -12.72^\circ$ (*l* 1, homogeneous) (*semicarbazone*, m.p. 155—156°, $[\alpha]_D^{15} +55.0^\circ$ in MeOH ; 2:4-dinitrophenylhydrazone, m.p. 137.5°, $[\alpha]_D^{15} +31.0^\circ$ in CHCl_3 ; oxime (syrup), $[\alpha]_D^{15} +10.97^\circ$ in MeOH). Further reduction (Pd sol) of (I) yields the cyclopentanol (II), b.p. 94°/12 mm., $\alpha_D^{15} -1.56^\circ$ (*l* 1, homogeneous) (3:5-dinitrobenzoate, m.p. 82—83°, $[\alpha]_D^{15} -2.0^\circ$ in CHCl_3), oxidised to the ketone, b.p. 80°/11 mm., $\alpha_D^{15} +9.94^\circ$ (*l* 1, homogeneous) (2:4-dinitrophenylhydrazone, m.p. 101.5°, $[\alpha]_D^{15} +60.0^\circ$ in CHCl_3 ; semicarbazone (amorphous), m.p. 135—137°, $[\alpha]_D^{15} +122.0^\circ$ in MeOH). Reduction (Pd sol) of *d*-sabinol yields (I), (II), an isomeride of (I), b.p. 95—96°/12 mm., $\alpha_D^{15} -4.66^\circ$ (*l* 1, homogeneous) [oxidised to the ketone, b.p. 88—90°/12.5 mm., $\alpha_D^{15} -28.0^\circ$ (*l* 1, homogeneous) (2:4-dinitrophenylhydrazone, m.p. 131°, $[\alpha]_D^{15} +14.0^\circ$ in CHCl_3)], thujyl alcohols, and thujane.

β -Thujone is reduced ($\text{Na}\cdot\text{EtOH}$) to a mixture of alcohols, converted by phthalic anhydride and $\text{C}_3\text{H}_5\text{N}$ into the *H* phthalate. The cinchonine salt of this on fractionation and hydrolysis yields *d*-isothujyl alcohol, oxidised to *d*-isothujone; the more sol. fraction when hydrolysed, and the product purified via the strychnine salt, gives *l*-neothujyl alcohol. This has the *cis*-H configuration, since it reacts more slowly than *l*-thujyl alcohol with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$.

A. LI.

Composition of the essence and heated oil of *Juniperus oxycedrus*. L. M. MOUSSERON, R. GRANGER, and M. RONAYROUX (Compt. rend., 1939, 208, 1411—1413).—Fractional distillation of the essence gives cadinene (I), b.p. 144°/20 mm. $[\alpha]_D^{20} +68.65^\circ$ (cf. Lepeschkin, A., 1908, i, 557) (*hydrochloride*, m.p. 116°), which when heated with S at 250°/2 hr. gives cadalene (II) (1:6-dimethyl-4-isopropyl-naphthalene) (*picrate*, m.p. 114°). (I) with Pt-H_2 gives tetrahydrocadinene, b.p. 142°/20 mm. Cadinol (III), b.p. 166°/20 mm., $[\alpha]_D^{20} -56.88^\circ$, present in large amount in the essence and to a smaller extent in the destructively distilled wood oil, when dehydrogenated gives (II) and is reduced (Pt-H_2) to dihydrocadinol (IV), b.p. 155°/20 mm. (III) or (IV) with Ac_2O at 100—150° gives a small yield (10—25%) of an acetate, which indicates that the OH is probably *tert*. Fractional distillation of the oil gives a dimethylnaphthalene, b.p. 133°/20 mm. (*picrate*, m.p. 105°), and a sesquiterpene, $\text{C}_{15}\text{H}_{24}$, b.p. 132°/20 mm. $[\alpha]_D^{20} -23.61^\circ$, reduced (Pt-H_2) to a compound,

$C_{15}H_{28}$, b.p. $130^{\circ}/20$ mm., and dehydrogenated to a hydrocarbon which affords no picrate. The essence also contains 5% of a sesquiterpene alcohol, $C_{15}H_{25}OH$, m.p. $118-119^{\circ}$, $[\alpha]_{579} -89.2^{\circ}$ in C_6H_6 , isomeric with (III).
J. L. D.

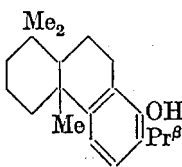
The sesquiterpene ketone from Lampoejang pait (*Zingiber amaricans*). A. G. VAN VEEN (Rec. trav. chim., 1939, 58, 691—706).—The mixture, $C_{15}H_{22}O$, m.p. 67° , of sesquiterpene ketones isolated from the roots of Lampoejang pait [*Z. zerumbet* (or *amaricans*)] by van Romburgh (1902) is re-investigated. An optically inactive mixture, m.p. $62-68^{\circ}$, is obtained which on crystallisation or distillation affords mixtures, m.p. 67° or 69° , respectively, of isomerides, $C_{15}H_{22}O$ (I). (I) gives a semicarbazone, $C_{16}H_{25}ON_3$ (II), m.p. $155-160^{\circ}$ (best prepared in C_5H_5N), and an oxime, $C_{15}H_{23}ON$, m.p. 179° ; both are mixtures. Hydrogenation (PtO_2 ; AcOH) of (I) (m.p. 68°) gives a mixture of ketones, b.p. $125-145^{\circ}/1.7$ mm., which affords fractions (III), m.p. 60° , mainly $C_{15}H_{30}O$ (aliphatic), and (IV), b.p. $125-133^{\circ}/0.2$ mm., mainly $C_{15}H_{28}O$ (monocyclic). (III) gives a semicarbazone, $C_{16}H_{33}ON_3$, m.p. 187° , and an oxime, $C_{15}H_{31}ON$, m.p. 105° . Prior chromatographic separation (Al_2O_3 ; light petroleum) of (I) gives a fraction, m.p. $65-66^{\circ}$, which is hydrogenated to an aliphatic ketone (V), $C_{15}H_{30}O$, m.p. 60° (semicarbazone, m.p. 187°), derived from a compound with 4 double linkings. (I) and Na-EtOH give a product, $C_{15}H_{28}O$, b.p. $\sim 130^{\circ}/0.1$ mm. (3:5-dinitrobenzoyl derivative, m.p. $\sim 112^{\circ}$) (oxidation with CrO_3 does not give the ketone, $C_{15}H_{26}O$), which with Se at 280° (24 hr.), then at $300-340^{\circ}$ (15 hr.), gives an oil, b.p. $140-160^{\circ}/30$ mm., giving only a trace of picrate. (I) and 50% H_2SO_4 -AcOH (in CO_2) at 60° give a product, $C_{15}H_{22}O$, b.p. $145-150^{\circ}/0.3$ mm. (semicarbazone, m.p. 165°), which is successively reduced and dehydrogenated to a product which affords no picrate or styphnate. No $C_{10}H_8$ derivative is obtained from any of the compounds described. (II) and NaOEt-EtOH at $180-190^{\circ}$ for 12 hr. afford a product, $C_{15}H_{24}$, b.p. $130^{\circ}/30$ mm. (IV) and $PhCHO$ -NaOEt, then $KHSO_4$, give a derivative, $C_{22}H_{34}O$, b.p. $180^{\circ}/0.2$ mm., ozonised ($CHCl_3$) to a product, b.p. $\sim 80^{\circ}/0.1$ mm.
A. T. P.

Triterpene resins and related acids. VI. C. W. PICARD, K. S. SHARPLES, and F. S. SPRING (J.C.S., 1939, 1045—1048; cf. A., 1939, II, 121).—The absorption spectrum of β -amyranonyl acetate (I) ("oxy- β -amyrin acetate," A., 1933, 1300) indicates the presence of an isolated CO group. Reduction ($Na + C_5H_{11}OH$) yields the diacetate, m.p. $183-184^{\circ}$, $[\alpha]_D^{25} +42.19^{\circ}$ in $CHCl_3$, of dihydroxy- β -amyrene, m.p. $216-217^{\circ}$, $[\alpha]_D^{25} +97.6^{\circ}$ in $CHCl_3$. (I) with Br and a trace of HBr in AcOH yields the acetate, m.p. $289-290^{\circ}$, $[\alpha]_D^{25} +73.7^{\circ}$ in $CHCl_3$, of iso- β -amyrenonol, $C_{30}H_{48}O_2$, m.p. $232-233^{\circ}$. Reduction ($Na + C_5H_{11}OH$) and acetylation of this acetate gives dehydro- β -amyrenyl acetate identical with that obtained by reduction of β -amyrenonol (A., 1938, II, 416). Me acetylketodihydro-oleanolate (Ruzicka *et al.*, A., 1937, II, 382) with Br and a trace of HBr in AcOH yields Me isoacetylketo-oleanolate (*idem.*, A.,

1939, II, 29). The implications of these results are discussed.
A. Li.

Lignin and related compounds. XL. Extraction of birch lignin with formic acid. M. LIEFF, G. F. WRIGHT, and H. HUBBERT (J. Amer. Chem. Soc., 1939, 61, 1477—1482; cf. A., 1939, II, 273).—Birch lignin, extracted by HCO_2H , is fractionated and compared with the product obtained by AcOH. Active H and CO (determined by $MgMeI$; higher in C_5H_5N than in dioxan), OMe, and O-CHO are determined for the various fractions as obtained and after methylation (Me_2SO_4 and CH_3N_2) and subsequent hydrolysis. The results are held to support the presence of guaiacyl and syringyl groups.
R. S. C.

Miro resin. I. Ferruginol. C. W. BRANDT and L. G. NEUBAUER (J.C.S., 1939, 1031—1037).—Miro resin contains 70% of a diterpenic resinol, ferruginol (I), $C_{29}H_{30}O$, b.p. $175^{\circ}/0.3$ mm., $[\alpha]_D^{25} +40.6^{\circ}$ in EtOH [formate, m.p. $96-97^{\circ}$; acetate, m.p. $81-82^{\circ}$, $[\alpha]_D^{25} +60.3^{\circ}$ in EtOH; benzoate, m.p. 154° ; Me ether (resinous), b.p. $163-166^{\circ}/0.3$ mm.]. (I) is slightly sol. in aq. NaOH, yields a brownish-green colour with $FeCl_3$, a deep red colour with p - SO_3H - C_6H_4 - N_2Cl , and gives the xanthoproteic reaction. Treatment of (I) with BzO_2H , and n of (I) and of its Me ether, indicate the presence of 3 double linkings. (I) absorbs 4 I, and 4, 6, or 8 Br per mol., according to conditions. Hydrogenation of (I) with PtO_2 in EtOAc gives a non-homogeneous product, $C_{26}H_{32}O$, but either (I) or its acetate with H_2 - PtO_2 in AcOH yields ferruginane, $C_{20}H_{36}$, b.p. $139-140^{\circ}/0.3$ mm., $[\alpha]_D^{25} +37.4^{\circ}$ in EtOH. (I) does not condense with maleic anhydride. Dehydrogenation (Se) of ferruginane gives retene, whilst (I) with Se yields a phenol (II), $C_{18}H_{18}O$, m.p. 178° (picrate, m.p. $176-177^{\circ}$; styphnate, m.p. 172° ; acetate, m.p. $90-91^{\circ}$) (with or without some pimanthrene, according to conditions). (II) is oxidised (CrO_3) to the acetate, m.p. $188-189^{\circ}$, of a hydroxyquinone, $C_{18}H_{16}O_3$, m.p. $284-285^{\circ}$, and when distilled in H_2 over hot Zn dust yields pimanthrene and 1-methylphenanthrene. Oxidation [KOH - $K_3Fe(CN)_6$] of the acetate of (II) yields naphthalene-1:5:6-tricarboxylic acid. It is concluded that (II) is 8-hydroxyretene, identical with the retinol of Keimatsu *et al.* (A., 1936, 1248), and that (I) has the appended formula.
A. Li.



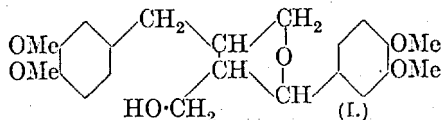
Constituents of "senso." VI. [Active constituents of the native toad, *Bufo vulgaris formosus*.] H. KONDO and S. OHNO (J. Pharm. Soc. Japan, 1938, 58, 15—18).—The isolation of ψ -deacetylbufotalin (I), $C_{24}H_{36}O_5$, through its amorphous Ac derivative is described. It has a distinct action on the heart. Many of its derivatives are amorphous but it yields a cryst. 3:5-dinitrobenzoate, m.p. $238-240^{\circ}$, and a p -nitrobenzoate, m.p. $226-227^{\circ}$, which depresses the m.p. of cinobufagin p -nitrobenzoate. Hydrolysis of (I) with 0.5N-KOH-EtOH gives a yellow solution indicating keto-enolic tautomerism within the mol. The lactone thus obtained gives an oxime which does not lose the N -OH group when treated with 0.5N-KOH-EtOH; it is

therefore probable that OH in (I) can be tautomerised since (I) does not react with NH_2OH unless it has been pre-treated with alkali. Catalytic hydrogenation (Pd, Pt, or PtO_2) of (I) causes absorption of nearly 3 H_2 with simultaneous production of acid. The spectrum of (I) is nearly identical with those of cinobufagin and gamabufogenin (II); (I) is therefore probably an enol-lactone although it does not give the colour reactions of Legal and Baljet.

Fat and α -cholesterol are removed from *Bufo vulgaris formosus* by light petroleum and (II) is extracted from the residue by CHCl_3 . The remainder is treated with 2% NaHCO_3 and then chromatographed, whereby a small amount of a cryst. sterol-like material, m.p. 244° , is isolated with an amorphous substance (III), $\text{C}_{26}\text{H}_{36}\text{O}_6$, which contains Ac and gives an amorphous acetate, $\text{C}_{26}\text{H}_{35}\text{O}_6\text{Ac}$ [with a small amount of (?) acetylbufotalin]. (III) with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ in $\text{C}_5\text{H}_5\text{N}$ affords two *p*-nitrobenzoates, $\text{C}_{25}\text{H}_{33}\text{O}_5\text{-CO-C}_6\text{H}_4\text{-NO}_2$, m.p. $286\text{--}287^\circ$, and $\text{C}_{26}\text{H}_{35}\text{O}_6\text{-CO-C}_6\text{H}_4\text{-NO}_2$, m.p. $171\text{--}178^\circ$. Pharmacologically (I) and (III) appear to be nearly identical. Suberic acid, bufotionin, and bufotoxin have also been isolated, so that the constituents are mainly identical with those of the European and Chinese toad.

H. W.

Constituents of natural phenolic resins. XV. Stereochemical relationship of lariciresinol and pinoresinol. R. D. HAWORTH and D. WOODCOCK (J.C.S., 1939, 1054—1057; cf. A., 1937, II, 202).—Reduction (H_2 , Pd-C, AcOH) (prep. of the Pd-C and reductions must be carried out in an all-glass apparatus) of *d*-lariciresinol Me_2 ether (I) gives $\beta\gamma$ -diveratrylbutane- $\alpha\delta$ -diol (II), m.p. $121\text{--}122^\circ$, $[\alpha]_D^{17} -26.2^\circ$ in CHCl_3 , which with KHSO_4 at 180° affords 3 : 4-diveratryltetrahydrofuran, m.p. $118\text{--}119^\circ$, $[\alpha]_D^{17}$



— 58.9° in CHCl_3 . (II) is oxidised by $\text{KMnO}_4\text{-COMe}_2$ to veratric acid (III), and by NaOBr-aq. dioxan to (III) and *l*-matairesinol Me_2 ether. *d*-Pinoresinol Me_2 ether (formula given) is reduced (H_2 , Pd-C, AcOH) to (I) or more completely to (II) (cf. Erdtmann, A., 1935, 627). Similar reduction of *l*-olivil Me_2 ether (IV) gives α -hydroxy- $\alpha\delta$ -di-(3 : 4-dimethoxyphenyl)- $\beta\gamma$ -di-(hydroxymethyl)butane, m.p. $137\text{--}138^\circ$, $[\alpha]_D^{17} -14.7^\circ$ in CHCl_3 , dehydrated by KHSO_4 , AcCl , or HCO_2H to intractable products. Reduction is limited to the benzyl ether linkings. The results show a common configuration for lariciresinol and pinoresinol; the 2 H attached to the di-propylbenzene junction are "cis" in both cases (cf. Erdtmann, A., 1937, II, 28). A "trans" arrangement is probable for (IV) and the lactonic lignans.

A. T. P.

Action of cyanogen bromide on furan. A. H. KLOPP and G. F. WRIGHT (J. Org. Chem., 1939, 4, 142—149).—Furan and CNBr at 100° (bath) give low yields of 2-furannitrile and 2-bromofuran (I), suggesting primary addition at positions 2 : 5 only, with subsequent elimination of HBr and HCN . In dioxan, at 25° for 8 days, 49% of (I) and 5% of 2 : 5-dibromo-

A. A. (A., II.)

furan are obtained (exclusive elimination of HCN). Theoretical aspects of the above and similar addition reactions are discussed.

A. T. P.

Nitrosation and nitration of 2- and 3-hydroxyfuran. H. H. HODGSON and R. R. DAVIES (J.C.S., 1939, 1013—1014).—Treatment of 2-hydroxyfuran in dil. NaOH with NaNO_2 , then HCl at 0° , gives 5-nitroso-, m.p. 176° , oxidised $[\text{KOH-K}_3\text{Fe}(\text{CN})_6]$ to 5-nitro-2-hydroxyfuran, m.p. 92° (also prepared by direct nitration). Both are reduced (Zn-HCl) to 5-amino-2-hydroxyfuran, m.p. 185° . 3-Hydroxyfuran similarly yields 2-nitroso-, m.p. 151° , 2-nitro-, m.p. 76° (prepared by oxidation, or by nitration in H_2SO_4 or Ac_2O), and 2-amino-3-hydroxyfuran, m.p. 92° .

A. LI.

Destruction of furfuraldehyde in presence of mineral acids. A. I. LAZAREV (Prom. Org. Chim., 1939, 6, 258—259).—Destruction of furfuraldehyde by boiling in H_2O with HCl , H_2SO_4 , NaCl , or CaCl_2 proceeds exponentially, at a rate \propto concn. of reagent.

R. T.

Egonol. IX. General synthetical method for the preparation of 2-phenylcoumarone and its derivatives and synthesis of egonol. S. KAWAI, T. NAKAMURA, and N. SUGIYAMA (Ber., 1939, 72, [B], 1146—1154).—Mainly an extended account of work already abstracted (A., 1939, II, 275). COMeEt is preferable to COMe_2 or EtOH for the condensation. Dihydroconiferyl alcohol is transformed by allyl bromide and anhyd. K_2CO_3 in boiling abs. EtOH into 4- γ -hydroxypropyl-6-allylguaiacol, b.p. $193\text{--}195^\circ/10$ mm., isomerised by aq. KOH at $170\text{--}175^\circ$ to 4- γ -hydroxy-*n*-propyl-6-propenylguaiacol, b.p. $209\text{--}211^\circ/10$ mm., m.p. 67° , from which styraxinic acid is obtained by ozonisation.

H. W.

Furano-compounds. II. R. T. FOSTER and A. ROBERTSON. **III. Euparin.** B. KANTHONG and A. ROBERTSON. **IV. Synthesis of allobergapten.** R. T. FOSTER, W. N. HOWELL, and A. ROBERTSON. **V. Synthesis of tetrahydroeuparin and the structure of euparin.** B. KANTHONG and A. ROBERTSON (J.C.S., 921—925, 925—930, 930—933, 933—936).—II. *O*-Dimethylphloroglucinolaldehyde and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ give $(\text{COMe}_2\text{-K}_2\text{CO}_3)$ *Et* 3 : 5-dimethoxy-2-formylphenoxyacetate (I), m.p. 105° (2 : 4-dinitrophenylhydrazones, m.p. 197°), hydrolysed to the acid, m.p. 177° , which with $\text{Ac}_2\text{O-NaOAc}$ affords 4 : 6-dimethoxycoumarone (II), b.p. $108\text{--}110^\circ/0.15$ mm. (picrate, m.p. 95°). Hydrogenation (Pd-C) of (II) yields 4 : 6-dimethoxycoumaran, m.p. 52° , not identical with the product prepared by Dean *et al.* (A., 1925, i, 280). HCl-HCN and (II) give in small yield 4 : 6-dimethoxy-7-formylcoumarone, m.p. 180° , reduced with H_2 (Pd-C) to the 7-methylcoumaran (III), m.p. 73° . Cyclisation (NaOEt) of (I) gives *Et* 4 : 6-dimethoxycoumarone-2-carboxylate, m.p. 96.5° , which with HCl-HCN affords the 7-formyl compound, m.p. 201° . 2-Hydroxy-4 : 6-dimethoxy-5-methylbenzaldehyde and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ yield $(\text{COMe}_2\text{-K}_2\text{CO}_3)$ *Et* 3 : 5-dimethoxy-2-formyl-4-methylphenoxyacetate, m.p. 92° (2 : 4-dinitrophenylhydrazones, m.p. 218°), cyclised (KOEt) to *Et* 4 : 6-dimethoxy-5-methylcoumarone-2-carboxylate, m.p. 115° , and 3 : 5-dimethoxy-2-formyl-4-methylphenoxyacetic acid, m.p. 172° . Hydrogenation

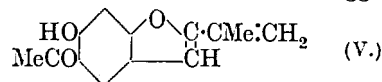
(Pd-C) of 6-hydroxy-2:4-dimethoxybenzaldehyde affords *s*-2:2'-dihydroxy-4:4':6:6'-tetramethoxydiphenylethane, m.p. 218°, and *C*-methylphloroglucinol α -Me₂ ether, converted through 2:3:4:6-OH·C₆HMe(OMe)₂·CHO into Et 3:5-dimethoxy-2-formyl-6-methylphenoxyacetate (2:4-dinitrophenylhydrazone, m.p. 198°). This ester is cyclised (KOEt) to Et 4:6-dimethoxy-7-methylcoumarone-2-carboxylate (IV), m.p. 127°, and 2:5-dimethoxy-2-formyl-6-methylphenoxyacetic acid, m.p. 163°. Hydrolysis of (IV) gives the corresponding acid, m.p. 242° (decomp.), decarboxylated to 4:6-dimethoxy-7-methylcoumarone, m.p. 38° (*picrate*, m.p. 110°), which is hydrogenated (Pd-C) to (III). 4:6-Dimethoxy-3-methylcoumaran, b.p. 91—92°/0.05 mm., is prepared by hydrogenation of 4:6-dimethoxy-3-methylcoumarone. Acetylation (Ac₂O-NaOAc) of 4:6-dimethoxy-2-methyl-3-coumaranone affords 4:6-dimethoxy-3-acetoxy-2-methylcoumarone, m.p. 69°. The presence of α -CO₂Et inhibits hydrogenation of the coumarone to the coumaran by a Pd catalyst.

III. Euparin (V), C₁₇H₁₆O₄, m.p. 118.5° [2:4-dinitrophenylhydrazone, m.p. 252°; *oxime*, m.p. 147—148°; *semicarbazone*, m.p. 255°; *acetate*, m.p. 80°; *O*-Me derivative (VI), m.p. 76—77°], has been isolated from the roots of *Eupatorium purpureum*. It is reduced (H₂-Pd-C) to tetrahydroeuparin, m.p. 71° (*acetate*, m.p. 96—97°; *oxime*, m.p. 133°; 2:4-dinitrophenylhydrazone, m.p. 240—241°), which forms an *O*-Me derivative, m.p. 57°; the *oxime*, m.p. 139°, of this derivative with SOCl₂ gives an *amide*, m.p. 133—134°, hydrolysed to the *amine*, m.p. 72°, which is re-acetylated to the *amide*. This affords proof of the presence of *C*-Ac in the *O*-Me compound. Oxidation of (VI) with KMnO₄ affords 2-hydroxy-4-methoxy-5-acetylbenzoic acid, m.p. 215—217° (decomp.), demethylated to the 2:4-(OH)₂-acid, and decarboxylated to 2-*O*-methylresacetophenone (2:4-dinitrophenylhydrazone, m.p. 216—217°), also obtained by debenzoylation of 2-methoxy-4-benzoyloxyacetophenone, m.p. 69°. Ozonolysis of (VI) leads to CH₂O and 2-hydroxy-4-methoxy-5-acetylbenzaldehyde, m.p. 117—118°. Condensation of (V) with maleic anhydride gives a *product*, m.p. 244—245°, and of (VI) affords a *product*, m.p. 212—213°. It is shown that (V) is a hydroxy-*C*-acetyl-coumarone or -chromen and possible formulae are suggested.

IV. 2:4:6-OH·C₆H₂(O·CH₂Ph)(OMe)·CHO and CH₂Br·CO₂Et give (K₂CO₃-COMe₂) Et 5-benzoyloxy-3-methoxy-2-formylphenoxyacetate, m.p. 74° (*acid*, m.p. 136°; 2:4-dinitrophenylhydrazone, m.p. 220°), which with NaOEt affords Et 6-benzoyloxy-4-methoxycoumarone-2-carboxylate, m.p. 111°, debenzylated to the 6-OH-ester, m.p. 193°. This ester and HCl-HCN yield Et 6-hydroxy-4-methoxy-7-formylcoumarone-2-carboxylate (VII), m.p. 178° (2:4-dinitrophenylhydrazone, m.p. 252°), which is catalytically reduced (Pd-C) and methylated (MeI) to Et 4:6-dimethoxy-7-methylcoumarone-2-carboxylate. Ac₂O-NaOAc and (VII) give Et 7-methoxy-5:6:4':5'-furocoumarin-2'-carboxylate, m.p. 240°. Hydrolysis (KOH-EtOH-H₂O) of (VII) leads to 6-hydroxy-4-methoxy-7-formylcoumarone-2-carboxylic acid, m.p. 281° (decomp.), which with Cu in quinoline gives 6-hydroxy-4-methoxy-7-formylcoumarone, m.p. 135° (2:4-dinitrophenylhydr-

azone, m.p. 253°). This aldehyde and CN·CH₂·CO₂H afford 7-methoxy-5:6:4':5'-furocoumarin-3-carboxylic acid, m.p. 242°, decarboxylated (Cu-quinoline) to 7-methoxy-5:6:4':5'-furocoumarin (*allobergapten*), m.p. 207°. 5-Benzoyloxy-3-methoxy-2-formylphenoxyacetic acid and Ac₂O-NaOAc yield 6-benzoyloxy-4-methoxycoumarone, m.p. 55—56°, debenzylated and hydrogenated (H₂-Pd-C) to 6-hydroxy-4-methoxycoumaran (*p*-nitrobenzoate, m.p. 159—160°).

V. Tetrahydroeuparin (VIII) and KOH give a small quantity of Bu^δCO₂H, and this appears to support the view that (VIII) is an isopropylcoumaran derivative. Reduction (Na-Hg-AcOH) of the *oxime*, m.p. 165—166°, of 6-hydroxy-2-isopropyl-3-coumaranone affords after heating in vac. 6-hydroxy-2-isopropyl-coumarone, m.p. 75—76°, hydrogenated (H₂-Pd-C) to the -coumaran, m.p. 79—80°. This compound and AcCN give 6-hydroxy-5-acetyl-2-isopropyl-coumaran, identical with a natural specimen of (VIII). 6-Acetoxy-2-isopropylcoumaran and AlCl₃ afford 6-hydroxy-7-acetyl-2-isopropylcoumaran, m.p. 115—116° (2:4-dinitrophenylhydrazone, m.p. 295—297°). 6-Hydroxy-2-*n*-propyl-3-coumaranone, m.p. 108—109°, prepared from α -bromo-*n*-valeryl chloride and resorcinol, gives an *oxime*, reduced (Na-Hg: small yield) to 6-hydroxy-2-*n*-propylcoumarone (*p*-nitrobenzoate, m.p. 61—62°). EtOAc and Na with (VIII) yield 6-hydroxy-5-acetoacetyl-2-isopropylcoumaran, m.p. 109—110°, cyclised (AcOH-HCl) to 2-methyl-2'-isopropyl-2':3'-dihydrofuro(4':5':6:7)chromone, m.p. 119—120°. Similar reaction with (V) gives 6-hydroxy-5-acetoacetyl-2-isopropylcoumarone, m.p. 139—140°, and 2-methyl-2'-isopropylfuro(4':5':6:7)chromone, m.p. 220°. The constitution for (V) is suggested.



F. R. S.

Diethyl 3:5-diacetyltetrahydropyran-3:5-dicarboxylate and diethyl 3-methyl-4-hydroxymethyl- Δ^2 -cyclohexenone-4:6-dicarboxylate. J. DECOMBE (Bull. Soc. chim., 1939, [v], 6, 1061—1066; cf. A., 1938, II, 100).—CH₂[C{Ac(CH₂·OH)·CO₂Et}₂] (Gault *et al.*, A., 1938, II, 216) and HCl (cold) give Et₂ 3:5-diacetyltetrahydropyran-3:5-dicarboxylate (I), m.p. 89—90° [HgCl₂ derivative, m.p. ~100° (decomp.)], and Et₂ 3-methyl-4-hydroxymethyl- Δ^2 -cyclohexenone-4:6-dicarboxylate (II), b.p. 194—195°/19 mm. (*oxime*) [dicarboxylic acid, m.p. 232—234° (decomp.)]. (I) and KOH-aq. EtOH give the Et H ester, m.p. 158°; (I) and aq. KOH at 100° (bath) afford the dicarboxylic acid, m.p. 289—290° (I) and MgMeI (4 mols.) give a *tert*-alcohol, C₁₆H₂₆O₇, m.p. 87—88°. (II) is formed probably by cyclisation of CO₂Et·C{Ac(CH₂·OH)·CH₂·CHAc·CO₂Et, from which larger yields of (II) can be obtained. A. T. P.

Synthesis of 3-aminocoumarin. K. C. PANDYA and T. S. SODHI (Current Sci., 1939, 8, 208—209).—*o*-OH·C₆H₄·CHO (1.5 mols.), NH₂·CH₂·CO₂H (1 mol.), and C₅H₅N (trace) at 140° (5 hr.) give 3-aminocoumarin (80% yield). S. H. H.

Synthesis of 4:5-dihydroxydiphenylene oxide. T. SHIMADA and K. HATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 18, 365—371).—2:6:2':6':

Tetrahydroxydiphenyl (I), m.p. 244° [prepared thus: $2:1:3\text{-NO}_2\text{-C}_6\text{H}_3(\text{OMe})_2 \rightarrow \text{NH}_2\text{-C}_6\text{H}_3(\text{OMe})_2 \rightarrow \text{C}_6\text{H}_3\text{I}(\text{OMe})_2 \rightarrow (\text{Cu at } 180^\circ) 2:6:2':6'\text{-tetramethoxydiphenyl, m.p. } 152^\circ, \rightarrow (\text{I})]$, with ZnCl_2 at 240–260° yields 4:5-dihydroxydiphenylene oxide, m.p. 215°, the absorption spectrum of which differs from that of the 2:7-isomeride. A. LI.

Halogen-substituted benzopyrylium salts. R. L. SHRINER and R. B. MOFFETT (J. Amer. Chem. Soc., 1939, 61, 1474–1477).—*p*-Bromo- ω -methoxyacetophenone (prepared in 54% yield from $\text{OMe-CH}_2\text{-CN}$ and *p*- $\text{C}_6\text{H}_4\text{Br-MgBr}$ in $\text{Et}_2\text{O-C}_6\text{H}_6$), m.p. 74–75.5°, *o*- $\text{OH-C}_6\text{H}_4\text{-CHO}$, and HCl in dry Et_2O give 4'-bromo-3-methoxyflavylum chloride, m.p. 105.5–107° (decomp.); the corresponding ferrichloride has m.p. 148–150°. 2:4:1-OH-C₆H₃Br-CHO, $\text{COPh-CH}_2\text{-OMe}$, and $\text{HCl-Et}_2\text{O}$ etc. give 7-bromo-3-methoxyflavylum ferrichloride, m.p. 182–185°. Br is not removed from the salts by "mol." Ag, AgNO_3 , AgCl , or NaOEt-EtOH , which excludes the quinonoid structures involving carbenium salts. Addition of aq. NaOCl-NaOH to the salts and H_2O_2 in COMe_2 or, less well, EtOH causes chemiluminescence. R. S. C.

Yellow colouring matter of *Dahlia variabilis*. J. R. PRICE (J.C.S., 1939, 1017–1018; cf. Schmid *et al.*, A., 1932, 621; 1933, 1168).—The pure colouring matter (extraction described), m.p. 211–213° (tetraacetate, m.p. 130–131°), gives an olive-brown colour with FeCl_3 , yields protocatechuic acid (I) and resacetophenone (II) (2:4-dinitrophenylhydrazones, m.p. 242–245°) when fused with KOH , condenses with resorcinol (for conditions cf. Robinson and Walker, A., 1934, 1226) giving 7:2':4'-trihydroxy-4-(3'':4'':dihydroxyphenyl)flavylum chloride (which gives a crimson quinone base, extracted by Et_2O), and is identical with butein synthesised from (I) and (II). A. LI.

Synthesis of 5:6-dihydroxyflavone and the structure of primetin. W. BAKER (J.C.S., 1939, 956–961).—2-Hydroxy-6-methoxyacetophenone is oxidised ($\text{K}_2\text{S}_2\text{O}_8\text{-NaOH}$) to the 2:5-dihydroxy-compound (I), m.p. 90°, benzoylated to the 2:5-(OBz)₂-derivative, m.p. 151–152°, and completely methylated (excess of $\text{Me}_2\text{SO}_4\text{-KOH}$) to 2:3:6-trimethoxyacetophenone, m.p. 41.5°. Bz₂O and NaOBz with (I) give, after hydrolysis, 5:6-dihydroxyflavone (II), m.p. 189–190° (Ac_2 derivative, m.p. 164°). Partial methylation of (I) affords 2-hydroxy-5:6-dimethoxyacetophenone, b.p. 162–163°/22 mm., benzoylated to the 2-OBz-compound, m.p. 87°, which with NaNH_2 yields 2-hydroxy-5:6-dimethoxydibenzoylmethane, m.p. 87°. This compound is cyclised (AcOH-NaOAc) to 5:6-dimethoxyflavone (III), m.p. 196°, demethylated to (II), and not the possible alternative 5:8-dihydroxyflavone. (II) and its derivatives differ from primetin (IV) and corresponding derived compounds, and a revision of the structure of (IV), hitherto regarded as (II), is therefore necessary. Partial demethylation (AlCl_3) of (III) gives 5-hydroxy-6-methoxyflavone, m.p. 128–129° (cf. Sugawara, A., 1934, 194). 7:8-Dihydroxyflavone forms a Me_2 ether under the conditions by which (IV) gives a Me ether, and 8-hydroxy-7-methoxyflavone, m.p. 227° (Ac derivative, m.p. 227°),

prepared from 2:3-dihydroxy-4-methoxyacetophenone, is different from the Me ether of (IV). (IV) is probably 5:8-dihydroxyflavone. F. R. S.

Constitution of naringin. Position of the sugar group. S. RANGASWAMI, T. R. SESHADRI, and J. VEERARAGHAVIAH (Proc. Indian Acad. Sci., 1939, 9, A, 328–332).—Methylation ($\text{MeI-COMe}_2\text{-K}_2\text{CO}_3$) of naringin followed by hydrolysis (HCl) gives 4-hydroxy-2:6:4'-trimethoxychalcone, m.p. 206–207°, indicating opening of the pyrone ring and methylation of all the phenolic OH, and establishing the presence of a disaccharide grouping attached to position 7 (cf. Asahina *et al.*, A., 1928, 1020). The chalcone can be prepared from 2:6-O-dimethylphloracetophenone and anisaldehyde. F. R. S.

Pigments of cotton flowers. VIII. Herbacintrin and quercimeritrin. P. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 365–369).—Methylation ($\text{Me}_2\text{SO}_4\text{-NaOH}$) of acetylherbacintrin, m.p. 222–224° (lit. 214–216°), followed by hydrolysis, gives 3:5:8:4'-tetramethylherbacintrin, thus indicating that herbacintrin is the 7-glucoside of herbacetin. Similar treatment of quercimeritrin acetate affords 3:5:3':4'-tetramethylquercetin. F. R. S.

Natural flavones. III. Structure of tambulin. P. K. BOSE and J. BOSE (J. Indian Chem. Soc., 1939, 16, 183–188).—Boiling MeOH extracts from the dry powdered fruit of *Zanthoxylum acanthopodium* an oil (I) from which light petroleum removes tambulin (II), $\text{C}_{18}\text{H}_{16}\text{O}_7$, m.p. 205° (yield 0.006%) [Ac_2 and (OMe)₂ (III) derivatives, m.p. 160–161° and 160°, respectively], which gives the colour reactions of a hydroxyflavone and is hydrolysed (20% EtOH-KOH ; 10 hr.) at 100° to *p*- $\text{OMe-C}_6\text{H}_4\text{-CO}_2\text{H}$. With HI (*d* 1.7) in PhOH at 130°/1.5 hr. (II) gives a product which gives Bargellini's test and therefore contains three contiguous OH groups in the 5:6:7-positions of the benzopyrone ring. (III) is different from tangeritin (cf. Goldsworthy and Robinson, A., 1937, II, 111), so that (II) may be 5:7-dihydroxy-4':6:8-trimethoxy- or 5:7-dihydroxy-4':3:8-trimethoxy-1:4-benzopyrone as herbacetin gives a positive Bargellini test (cf. Rao and Seshadri, A., 1939, III, 219). A MeOH solution of (I) deposits tambulol, m.p. 265–267° (acetate, m.p. ~120°). J. L. D.

Spectrographic examination of flavone pigments. B. SKARZYŃSKI (Biochem. Z., 1939, 301, 150–169).—The effect on the ultra-violet absorption spectrum of flavone and 2:3-dihydroflavone of the introduction of OH, OMe, and OAc groups has been examined and curves have been plotted. These exhibit max. in the zones 2900–3800 and 2260–2850 Å. The general form of the curves is determined by the benzopyrone structure. Possibly the spectra may be of use in the identification and determination of naturally occurring flavones. W. McC.

Picrotoxin. III. J. C. HARLAND and A. ROBERTSON (J.C.S., 1939, 937–943).—Reduction of picrotoxinone and of picrotoxinonic acid with HI-P gives a mixture from which a phenolic ketone (I), $\text{C}_{13}\text{H}_{16}\text{O}_2$, m.p. 189° (2:4-dinitrophenylhydrazones, m.p. 268°; semicarbazones, m.p. 201°), norpicrotic acid, $\text{C}_{11}\text{H}_{16}\text{O}_4$,

m.p. 113° (*Et* ester, b.p. 165°/0.01 mm.; *Me* ester, m.p. 61°), and *hydroxynorpicrotic acid*, m.p. 213° (*Et* ester, m.p. 125°; *methoxynorpicrotic acid*, m.p. 177°, and its *Me* ester, m.p. 93°), have been isolated. Reduction (Zn-Hg-EtOH-HCl) of (I) affords 2-hydroxy-1-methyl-4-ethyl-5:6:7:8-tetrahydronaphthalene (II), m.p. 66-5° (p-nitrobenzoate, m.p. 85°). 5-Methyl-2-ethylanisole, $(\text{CH}_3\text{CO})_2\text{O}$, and AlCl_3 yield β -3-methyl-6-ethylanisoylpropionic acid, m.p. 107° (semicarbazone, m.p. 186°), which is reduced (Zn-Hg-HCl) to γ -3-methyl-6-ethylanisylbutyric acid, m.p. 71-5°, cyclised to 2-methoxy-4-methyl-1-ethyl- α -tetralone, m.p. 75-5-76° (semicarbazone, m.p. 160°); this ketone is reduced and demethylated to 2-hydroxy-4-methyl-1-ethyl-5:6:7:8-tetrahydronaphthalene, m.p. 67°. 2:1:4-OMe- $\text{C}_6\text{H}_4\text{MeCOMe}$ (semicarbazone, m.p. 205°) is reduced to the -4-Et compound, which with $(\text{CH}_3\text{CO})_2\text{O}$ and AlCl_3 gives β -2-methyl-5-ethylanisoylpropionic acid, m.p. 129° (semicarbazone, m.p. 183°), reduced to γ -2-methyl-5-ethylanisylbutyric acid, m.p. 63°. Cyclisation (H_2SO_4) of this acid affords 2-methoxy-1-methyl-4-ethyl- α -tetralone, m.p. 64° (semicarbazone, m.p. 208°), which is reduced to 2-methoxy-1-methyl-4-ethyl-5:6:7:8-tetrahydronaphthalene, b.p. 112-116°/0.1 mm., demethylated to (II). From the structure of (II) the positions of the ethylenic linking and of an O in picrotoxinin and picrotoxic acid are deduced. The possible significance of the formation of a C_{10}H_8 derivative from a picrotoxinin degradation product is discussed and structural formulæ for nor- and hydroxynorpicrotic acid have been developed. F. R. S.

Leguminous insecticides of the Belgian Congo. E. CASTAGNE (Separate, Brussels, 1938, 102 pp.).—Rotenone and *dl*-toxicarol, and, by the action of alkali, deguelin and tephrosin, are obtained from the roots, pods, seeds, and leaves of *Tephrosia toxicaria*, *candida*, *vogelii*, and *virginiana*, leguminous insecticides indigenous to the Belgian Congo. The pods of *T. toxicaria* also contain tephrotoxin, $\text{C}_{17}\text{H}_{14}\text{O}_9\cdot\text{OMe}$, m.p. 163°, $[\alpha]_D^{25} -43.6^\circ$ in C_6H_6 . The roots of *Lonchocarpus sericans* contain lonchocarpin, $\text{C}_{23}\text{H}_{19}\text{O}_3$, m.p. 89°, $[\alpha]_D^{25} -8.33^\circ$ in C_6H_6 .

S. H. H.

Acyl derivatives of dibenzthiophen. II. A. BURGER and H. W. BRYANT (J. Org. Chem., 1939, 4, 119-122; cf. Gilman *et al.*, A., 1939, II, 33).—1-Acetyldibenzthiophen (I), m.p. 129-130°, isolated during the prep. of the 3-isomeride (II) (A., 1939, II, 34), is oxidised (method: Fuson *et al.*, A., 1934, 990) to dibenzthiophen-1-carboxylic acid, m.p. 261-262° (decomp.) (cf. Gilman, *loc. cit.*). Neither the oxime (III), m.p. 155-156°, nor the oxime acetate, m.p. 142-143°, from (I) gives chelated metallic derivatives. (III) rearranges (Beckmann) to 1-acetamidodibenzthiophen, m.p. 195-197°. (I) or (II) (more readily) and $\text{Br-Et}_2\text{O}$ (exposed to sunlight in presence of HCl) give 1-, m.p. 149-151°, and 3- ω -bromoacetyldibenzthiophen (IV), m.p. 115-116°, converted by piperidine in C_6H_6 into the respective piperidino-derivatives [hydrochlorides have m.p. 253-260° (decomp.) (sinters at 250°) and 245-246° (decomp.) (sinters at 242°), respectively]. (IV) and NH_4Et_2 yield 3-(diethylaminoacetyl)dibenzthiophen, m.p. 200-202° (decomp.). 3-Bromodibenzthiophen and $\text{Cu}_2(\text{CN})_2$ at

240-270° give 3-cyanodibenzthiophen, m.p. 159-160° (IV) and $\text{CHNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 , followed by hydrolysis with KOH-EtOH , and decarboxylation by heating at 150-160°, afford 3-succinyldibenzthiophen (γ -keto- γ -3-dibenzthienylbutyric acid) (cf. Gilman), of which the structure is thus confirmed.

A. T. P.

Thioindigo synthesis. IV. Synthesis of 5:6:5':6'- and 6:7:6':7'-tetrachloro-4:4'-dimethylthioindigo. R. SHIBATA and H. UMEJIMA. V. Nitro-derivative of 6:6'-dichloro-4:4'-dimethylthioindigo. R. SHIBATA, T. SASA, and H. UMEJIMA (J. Soc. Chem. Ind. Japan, 1939, 42, 37-38B, 38B; cf. A., 1936, 1387).—IV. 5:6:5':6'-(I) (violet) and 6:7:6':7'-tetrachloro-4:4'-dimethylthioindigo (II) (red-violet) are synthesised from 5:6:1- and 3:6:1- $\text{C}_6\text{H}_3\text{ClMe}\cdot\text{NH}_2$ thus: $\text{C}_6\text{H}_3\text{ClMe}\cdot\text{NH}_2 \rightarrow \text{C}_6\text{HCl}_2\text{Me}(\text{NH}_2)\cdot\text{SH} \rightarrow \text{C}_6\text{HMeCl}_2(\text{NH}_2)\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (inner salts, m.p. 158-159° and 231°) $\rightarrow \text{C}_6\text{HCl}_2\text{Me}(\text{CO}_2\text{H})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow$ dichloromethylthioindoxyl (m.p. — and 140-142°, respectively) \rightarrow (I) and (II).

V. 6:6'-Dichloro-4:4'-dimethylthioindigo with conc. H_2SO_4 and powdered KNO_3 gives an orange-red $(\text{NO}_2)_2$ -derivative.

A. LI.

Configuration of the tervalent nitrogen atom. J. D. C. MOLE and E. E. TURNER (Chem. and Ind., 1939, 582).—In order to investigate the possibility of mol. dissymmetry dependent on the presence of non-coplanar N^{III} in 3-membered rings or *cis-trans*-isomerism due to the same cause, compounds of the type $\text{CR}_2\text{CH}_2\text{NR}'$, in which R' is a radical containing a salt-forming group remote from N, have been optically examined.

F. R. S.

l-Laurylpiperidine.—See B., 1939, 647.

Condensation of amino-ethers with naphthols, cresols, and naphthylamines. H. F. TSEOU and C. T. YANG (J. Org. Chem., 1939, 4, 123-127).—Piperidinomethyl Et ether (I) reacts with α - and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ at room temp., and with *o*-, *m*-, and *p*-cresol, and α - and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, at 100°, to give 1-hydroxy-4-, m.p. 133° (picrate, m.p. 98°), and 2-hydroxy-1-piperidinomethylnaphthalene, m.p. 96° (picrate, m.p. 101°), 5-piperidinomethyl-*o*-, b.p. 156-157°/6 mm. (picrate, m.p. 177°; platinichloride, m.p. 194°), 6-piperidinomethyl-*m*-, m.p. 56° (picrate, m.p. 127°), and 3-piperidinomethyl-*p*-cresol, m.p. 45° (picrate, m.p. 149°; platinichloride, m.p. 199°), and 1-amino-4-, m.p. 124°, and 2-amino-1-piperidinomethylnaphthalene, m.p. 114°, respectively. With NH_2Ph , NH_2Bz , and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ (I) reacts with H attached to N.

A. T. P.

Phenacylpicolinium chloride and *p*-phenylphenacylpyridinium chloride.—See B., 1939, 781.

Formation of 2:5-dihydroxypyridine by the action of hydroxylamine on furfuraldehyde. K. Aso (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 177-179).—Furfuraldehyde with $\text{NH}_2\text{OH}\cdot\text{HCl}$ or $\text{N}(\text{SO}_3\text{Na})_2\cdot\text{OH}$ at 155-160° under pressure yields 2:5-dihydroxypyridine. The mechanism is discussed.

A. LI.

Products of heating furfuraldehyde and hydrazine sulphate in an autoclave. K. Aso (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 180—181).—Furfuraldehyde and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ at 152—153° under pressure yield 3-hydroxy- and 2:5-dihydroxypyridine. The mechanism is discussed. A. Li.

Formation of 5-hydroxy-2-methylpyridine by the action of ammonium sulphate on 5-methylfurfuraldehyde. K. Aso (Bull. Inst. Phys. Chem. Res. Japan, 1939, 18, 182—184).—5-Methylfurfuraldehyde with $(\text{NH}_4)_2\text{SO}_4$ at 160° under pressure yields 5-hydroxy-2-methylpyridine. The mechanism is discussed. A. Li.

Specific colour reaction of adermin. R. KUHN and I. Löw (Ber., 1939, 72, [B], 1453—1457).—Under defined conditions 0.02—0.08 mg. of adermin (I) can be determined by the Folin-Denis method, but the blue solutions readily become turbid or give white ppts. 3-Hydroxypyridine (II) behaves similarly whereas PhOH invariably gives transparent, blue solutions. The replacement of saturated aq. Na_2CO_3 by 1% LiOH is advantageous; with saturated aq. Li_2CO_3 the reaction is too slow. Although (II) can be readily determined colorimetrically by coupling with diazotised $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, the yellow colour given with this reagent by (I) is too unstable. Since both reactions are given generally by phenols and also by many NH_2 -acids they are not sufficiently sp. to be used for the detection of (I) in biological solutions. (I) and (II) do not give the Vongerichten reaction with 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ or the König change with CNBr and benzidine and hence do not interfere with the determination of nicotinamide with these reagents. (I), 4-deoxyadermin, and 4-hydroxy-2:6-dimethylpyridine are determined by conversion by CH_2N_2 into their *O*-Me ethers, which are transformed into quaternary pyridinium salts by addition of MeI , Me_2SO_4 , or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$. A trace of the salt is treated with 2 or 3 drops of a solution of Na in EtOH and after 10—20 sec. a few drops of CHCl_3 are added, when a violet colour develops in the cold solution. The limit of sensitivity is reached with ~0.1 mg. of adermin hydrochloride. 3-Methoxy-2:4-dimethyl-5-hydroxymethyl-, m.p. 152°, and 3-methoxy-2-methyl-4:5-dihydroxymethyl-, (III), m.p. 125—126°, -pyridinium methiodide are described. $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ condenses with (III) in boiling EtOH containing piperidine to 3-methoxy-2- p' -dimethylaminostyryl-4:5-dihydroxymethylpyridinium methiodide, which gives an orange solution not particularly characteristic of (I). Unlike nicotinamide methiodide, (III) does not give the "yellow stage" with $\text{Na}_2\text{S}_2\text{O}_4$ under N_2 . H. W.

Synthesis of 2-pyridyldialkylcarbinols. B. EMMERT and E. ASENDORF (Ber., 1939, 72, [B], 1188—1194).—Gradual addition of HgCl_2 dissolved in COMeEt to Mg turnings in anhyd. $\text{C}_5\text{H}_5\text{N}$ affords 2-pyridyldimethylcarbinol, b.p. 88—90°/12 mm., 203—205°/atm. pressure, m.p. 49—50° (hygroscopic hydrochloride; picrate, m.p. 87.5°; methiodide, m.p. 103—104°), identical with the compound obtained from Et picolinate and MgMeI and converted by conc. H_2SO_4 at 120° into 2- α -methylvinylpyridine, b.p. 172—176°. MgMeI and Et isonicotinate afford

4-pyridyldimethylcarbinol, m.p. 136°. Analogously COMeEt yields 2-pyridylmethylethylcarbinol, b.p. 99—104°/15 mm., 216—220°/atm. pressure (platinichloride, m.p. 186°). COPhMe affords 2-pyridylphenylmethylcarbinol, b.p. 301—303°, m.p. 32° (picrate, m.p. 174° after slight softening), transformed by conc. H_2SO_4 at 100° into 2- α -phenylvinylpyridine, b.p. 288—292° (slight decomp.) (picrate, m.p. 151°); COPh_2 yields 2-pyridyldiphenylcarbinol, m.p. 104° [picrate, m.p. 173° (decomp.)]. 2-Methylpyridine and COMe_2 give 6-methyl-2-pyridyldimethylcarbinol, b.p. 98—100°/14 mm., whilst 4-methylpyridine gives 3(or 5)-methyl-2-pyridyldimethylcarbinol, b.p. 106°/14 mm. The mechanism of the reaction is discussed.

H. W.

[Synthesis in] the series of hydroxy- and alkoxy-oxindoles. G. HAHN and H. J. SCHULZ (Ber., 1939, 72, [B], 1308—1313).—Gradual addition of 3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ to conc. HNO_3 at 0° yields the 6- NO_2 -derivative, m.p. 207—208° (yield 67.5%), also produced (yield 67.5%) by the hydrolysis of 6-nitro-3:4-dimethoxyphenylacetamide (I), m.p. 224—225°, prepared from conc. HNO_3 and 3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ at 0°. α -Chloro-6-nitro-3:4-dimethoxyphenylacetamide, m.p. 86° (decomp.) after becoming discoloured, is derived from 3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot\text{CO}\cdot\text{NH}_2$. Reduction (Adams' Pd in AcOH) of (I) or (II) leads to 5:6-dimethoxyoxindole, m.p. 204—205°, converted by NaNO_2 and AcOH into 5:6-dimethoxyisatin-3-oxime, m.p. 213—214°. H. W.

Synthesis of ring compounds containing nitrogen. X (III). Synthesis of indole derivatives. I. New synthesis of indole. S. SUGASAWA, I. SATODA, and J. YANAGISAWA (J. Pharm. Soc. Japan, 1938, 58, 29—31).—Oxindole, obtained in 85% yield by heating $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NHPh}$ (1 part) with AlCl_3 (1.8 parts) at 225°, is converted by P_2S_5 under xylene at 100—110° into thio-oxindole, m.p. 145°, which dissolves in cold alkali hydroxide to a solution from which it cannot be pptd. unchanged by acid. It is electrolytically reduced at a Pb cathode to indoline, which when melted with $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and Pd -black at 120—125° gives indole. H. W.

Local anæsthetic action of substances of the quinoline-4-carboxylic acid series. I. S. I. LURIE (J. Gen. Chem. Russ., 1939, 9, 287—298).—The Na salts of 2- R -substituted quinoline-4-carboxylic acids with chlorodialkylaminoparaffins in xylene yield the following esters: β -diethylaminoethyl, $R = \text{Ph}$, 185—186°, $R = \text{OEt}$, m.p. 170—170.5°, $R = \text{OPr}^a$, m.p. 169.5—170.5°, $R = \text{OBu}^a$, m.p. 149°, $R = \text{OBu}^b$, m.p. 152—153°, $R = \text{isoamyl}$, m.p. 160—161°; γ -diethylaminopropyl, $R = \text{Ph}$, m.p. 178—179°, $R = \text{OEt}$, m.p. of citrate 99—100°, $R = \text{OPr}^a$, m.p. 136°, $R = \text{OBu}^a$, b.p. of base 207—211°/2.5 mm., m.p. of citrate 115—116°; γ -dimethylamino- β -dimethylpropyl, $R = \text{Ph}$, m.p. 176—177° (m.p. of base 44—46°), $R = \text{OEt}$, m.p. 115—116° (b.p. of base 207°/3 mm.), $R = \text{OPr}^a$, m.p. 123—124°, $R = \text{OBu}^a$, m.p. 137—138° (b.p. of base 207—210°/3 mm.); γ -dimethylamino- $\alpha\beta$ -dimethylpropyl, $R = \text{OBu}^a$, b.p. of base 214—217°/3 mm., m.p. of citrate 78—79°; unless otherwise specified the m.p. given

refer to the hydrochlorides. The anæsthetising action of the esters on rabbit cornea is $>$ of novocaine, but $<$ of cocaine. The esters cause irritation of the conjunctiva. Their activity and toxicity vary according to the nature of the base and R. R. T.

Utilisation of aryloxy-ketones in the synthesis of quinolines by the Pfitzinger reaction. P. K. CALAWAY [with H. R. HENZE] (J. Amer. Chem. Soc., 1939, **61**, 1355—1358).— COArMe and isatin in 33% aq. KOH at 100° give 3-aryloxyquinaldine-4-carboxylic acids (without the 2-aryloxymethyl isomerides), which resist reduction by red P-HI, but are decarboxylated by heating, usually at 250 – 260° . Thus are prepared 3-*phenoxy*- (I), m.p. 259.4° (decomp.), 3- α -*naphthoxy*- (II), m.p. 265.5° (decomp.), and 3-*thymoxy*-2-methylquinoline-4-carboxylic acid, m.p. 228° (decomp.), 3-*phenoxy*-, m.p. 72.2° , b.p. 130 – $140^\circ/8$ – 10 mm. [hydriodide, m.p. 126 – 130° , obtained from (I) by HI; picrate, m.p. 192 – 193°], 3- α -*naphthoxy*-, m.p. 102° (picrate, m.p. 208 – 209°), and 3- β -*naphthoxy*-2-methylquinoline, m.p. 95 – 96.5° (picrate, m.p. 205.8 – 206.8°). The structure of (II) and thus, by analogy, of the other products is proved by fission (and decarboxylation) by conc. HCl at 220° to give 3-hydroxyquinaldine (III). With $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ at 200 – 210° , (II) gives a *phthalone*, m.p. 243 – 245° , and with 1:1 conc. HNO_3 – H_2O at 100° gives a 4'- NO_2 -derivative, m.p. 221° (decomp.), converted by conc. HCl at 210° into (III) and 4:1- NO_2 - C_{10}H_6 -OH. $\text{COMe}\cdot\text{CH}_2\cdot\text{OPh}$, b.p. $115/2$ mm., is obtained in 53% yield by adding first Na and then $\text{COMe}\cdot\text{CH}_2\cdot\text{Br}$ (IV) to PhOH in C_6H_6 . α -, an oil, and β - $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{COMe}$, m.p. 78.4° , are obtained by adding first $\text{C}_{10}\text{H}_7\cdot\text{OH}$ and then (IV) to aq. NaOH. 2-*Thymoxyacetone*, b.p. 115 – $117/3$ mm., is prepared by adding (IV) to thymol in aq. NaOH. M.p. are corr. R. S. C.

isoQuinoline series. III. 1-Chloroalkyl-quinolines and their derivatives. B. B. DEY and T. R. GOVINDACHARI (Arch. Pharm., 1939, **277**, 177–192; cf. A., 1937, II, 389).—The Cl of 1- α -chloroalkyl-3:4-dihydroisoquinolines can be exchanged for OH or CN, but not for NH_2 or NR_2 ; it is eliminated by hydrogenation. Piperonal (20 g.) yields successively 3:4-methylenedioxyphenyl-acrylic (22 g.), m.p. 247° , and -propionic acid (17 g.), m.p. 87° , the amide (13 g.), m.p. 122° , of the latter acid, and homopiperonylamine (I) (6.5 g.), b.p. $200/30$ mm. ($\text{CH}_2\text{Cl}\cdot\text{CO}$) $_2\text{O}$ (modified prep. from AcOH and PCl_5), b.p. 128 – $130/25$ mm., in CHCl_3 then gives *chloroacethomopiperonylamine*, m.p. 71° , which with hot POCl_3 yields 6:7-methylenedioxy-1-chloromethyl-3:4-dihydroisoquinoline (II), m.p. 109° (decomp.) (hydrochloride, m.p. 190° ; methiodide, m.p. 230° ; picrate, m.p. 180°). Zn dust in $2\text{N}\cdot\text{H}_2\text{SO}_4$ eliminates the Cl from (II), yielding 6:7-methylenedioxy-1-methyl-1:2:3:4-tetrahydroisoquinoline, an oil (picrate, m.p. 185° ; hydrobromide, m.p. 268°), also obtained from (I) by successive treatment with Ac_2O , POCl_3 , and $\text{Zn}\cdot\text{H}_2\text{SO}_4$. Only oils are obtained from (II) by NH_3 etc. or NH_2Ph , and Mg does not react. With NaOH–EtOH at 50° (II) gives 6:7-methylenedioxy-1-hydroxymethyl-3:4-dihydroisoquinoline, m.p. 215° (acetate and benzoate could not be purified), reconverted into (II) by POCl_3 at 100° . With KCN–

EtOH, (II) gives 6:7-methylenedioxy-1-cyanomethyl-3:4-dihydroisoquinoline (III), m.p. 187° [vanillylidene, sinters at 230° , m.p. 250° (hydrochloride, sinters at 250° , m.p. 255°), benzylidene, sinters at 160° , m.p. 180° (hydrochloride, m.p. 204°), and piperonylidene derivative, m.p. 268 – 269° (hydrochloride, sinters at 259° , m.p. 265°), hydrolysed when reduced, even by H_2 –Pt], reduced by Zn dust in $4\text{N}\cdot\text{H}_2\text{SO}_4$ to 6:7-methylenedioxy-1-cyanomethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 93° (picrate, m.p. 190° ; hydrochloride, m.p. 254° ; methiodide, m.p. 215° ; Ac, m.p. 139° , and NO-derivative, m.p. 138°). Attempted hydrolysis of the CN of (III) by H_2O_2 yielded AcOH and 1-keto-6:7-methylenedioxy-1:2:3:4-tetrahydroisoquinoline, m.p. 183° (cf. Perkin, J.C.S., 1890, **57**, 992), reduced by Na–EtOH to 6:7-methylenedioxy-1:2:3:4-tetrahydroisoquinoline, which is also obtained from $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CHO}$ by POCl_3 , followed by $\text{Zn}\cdot\text{H}_2\text{SO}_4$. 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot[\text{CH}_2]_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CMe}\cdot\text{OH}$ (prep. from the base by $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ at 180°) and POCl_3 give 6:7-methylenedioxy-1- α -chloroethyl-3:4-dihydroisoquinoline, an oil (picrate, m.p. 184° ; methiodide, m.p. 275°), reduced by $\text{Zn}\cdot\text{H}_2\text{SO}_4$ to 6:7-methylenedioxy-1-ethyl-1:2:3:4-tetrahydroisoquinoline, an oil (picrate, m.p. 207° ; hydrochloride, m.p. 240°), which is also obtained from (I) and $(\text{EtCO})_2\text{O}$, followed by POCl_3 and $\text{Zn}\cdot\text{H}_2\text{SO}_4$. The 1- α - NH_2 -derivative could not be prepared. By methods outlined above are obtained 6:7-methylenedioxy-, an oil (picrate, m.p. 178°), and 6:7-dimethoxy-1- α -cyanoethyl-3:4-dihydroisoquinoline (picrate, m.p. 186°), 6:7-dimethoxy-1- α -chloroethyl-3:4-dihydroisoquinoline, an oil (picrate, m.p. 175° ; methiodide, m.p. 260°), and 6:7-dimethoxy-1-ethyl-1:2:3:4-tetrahydroisoquinoline, an oil (picrate, m.p. 186° ; hydrochloride, m.p. 214°). R. S. C.

Electrolytic reduction of naphthalimide and its derivatives. B. SAKURAI (Bull. Chem. Soc. Japan, 1939, **14**, 173–178).—Naphthalimide could not be reduced with a Pb cathode, but with Zn–Hg, 8% of hydrobenzisoquinoline [platinichloride, m.p. 198° (decomp.)] was obtained. *N*-Methyl- and -ethyl-naphthalimide in dil. H_2SO_4 with a Pb cathode yield respectively *N*-methyl- and -ethyl-naphthalimidine [platinichlorides, m.p. 172° (decomp.) and 165° (decomp.), respectively]; with Zn–Hg, *N*-methyl- and -ethyl-hydrobenzisoquinoline [platinichlorides, m.p. 212° (decomp.) and 197° (decomp.), respectively] and smaller amounts of the naphthalimidines are formed.

A. LI.

Methylated and methoxylated 5-chloro-acridines and -acridones and 10-methylacridones. K. GLET and S. NITZSCHE (J. pr. Chem., 1939, [ii], **153**, 200–224).—3:1:2- $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ is converted (Sandmeyer) into 3-chloro-*o*-toluic acid, m.p. 108° , transformed by boiling NH_4Ph (K_2CO_3 –Cu-bronze) into 3-methyldiphenylamine-2-carboxylic acid, m.p. 145° (decomp.). 5-Methyl-, m.p. 193 – 194° , and 6-methoxy-, m.p. 198° , -diphenylamine-2-carboxylic acid are described. Ring-closure of the requisite diphenylamine-2-carboxylic acids by POCl_3 leads to the following 5-chloro-acridines; -4-methyl-, m.p. 95 – 96° ; -2-methyl-, m.p. 125° ; -1-methyl-, m.p. 96 – 97° .

5-Chloro-4-methoxyacridine, m.p. 146—147°, from 4-methoxyacridone and POCl_3 , and 5-chloro-1-methoxyacridone, m.p. 128—130°, from 2'-methoxydiphenylamine-2-carboxylic acid and POCl_3 , appear new. Among substituted chloroacridines solubility and readiness of hydrolysis appear to run parallel. The prep. of 10-methylacridones is discussed and a new method, depending on the change between Me_2SO_4 and the 5-chloroacridines, is given. The following are new: 4-methylacridone, m.p. 315°; 4-methoxyacridone hydrochloride; 4:10-dimethylacridone, m.p. 141°; 3:10-, m.p. 150—151° (also monohydrate), and 2:10-, m.p. 188° (also monohydrate), -dimethylacridone; 4-, m.p. 164°, 3-, m.p. 147°, and 2-, m.p. 185°, -methoxy-10-methylacridone.

H. W.

Methylated and methoxylated 10-methylthioacridones and 10-methylacridoneanils. K. GLEU and S. NITZSCHE (J. pr. Chem., 1939, [ii], 153, 225—232).—The use of PCl_5 in addition to POCl_3 in the conversion of 10-methylacridones into 5-chloro-10-methylacridinium chlorides is unnecessary and frequently disadvantageous. The primary products are acridone- POCl_3 compounds which are readily and almost quantitatively converted by an excess of alkali H sulphide in EtOH into 10-methylthioacridones. There appears to be a remarkable parallelism between the depth of colour of these substances and the rate of hydrolysis of the corresponding 5-chloroacridines in acid solution. An explanation based on mesomerism is advanced. The following are new: 4:10-, m.p. 130°, 3:10-, m.p. 220°, 2:10-, m.p. 240°, and 1:10-dimethyl-, m.p. 158°, 4-, m.p. 122°, 3-, m.p. 186°, 2-, m.p. 227°, and 1-methoxy-, m.p. 114°, -10-methyl-thioacridone; 10-methylthioacridone, m.p. 263°; 4:10-, m.p. 177°, 3:10-, m.p. 121°, 2:10-, m.p. 114°, and 1:10-dimethyl-, m.p. 139—140°, 4-, m.p. 174—175°, 3-, m.p. 128—129°, 2-, m.p. 120—121°, and 1-methoxy-10-methyl-, m.p. 165—166°, -acridoneanil.

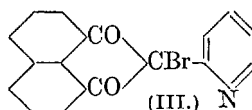
H. W.

10-Substituted thio- and seleno-acridones. K. GLEU and R. SCHAARSCHMIDT (Ber., 1939, 72, [B], 1246—1256).—Attempted isomerisation of S-methylthioacridones gives ill-defined results. The interaction between 10-methyl- or 10-ethyl-acridone and P_2S_5 in C_6H_6 does not occur sufficiently smoothly to be utilisable in the prep. of thioacridones. 10-Methylthioacridone is obtained by melting 10:10'-dimethyl-diacridene with S; the change is probably general. Thioacridones are readily obtained by the addition of alkali H sulphide in EtOH to the additive compounds of acridones and POCl_3 , whereby the products are usually pptd. Alternatively, a moderate excess of aq. $\text{Na}_2\text{S}_2\text{O}_3$ is added to the solution of the acridone in POCl_3 which has been heated and then cooled in ice. The colour of 10-substituted thioacridones (I) is very similar to that of the parent compound (II) so that the latter is almost exclusively a thioketone; the salts are probably derived from the tautomeric thiol form. When boiled with AcOH containing Cu powder (I) give a permanganate-like colour which withstands protracted boiling whilst (II) gives a red-violet solution which is completely decolorised by short boiling. Cu^{II} salts are without action whereas

Cu^{I} compounds yield Cu_2S . 10-Substituted acridones yield diacridylum salts or diacridenes when reduced by Zn and acid whereas (I) give dihydrodiacridenes. Addition of Se to acridene with formation of selenoacridone does not seem to occur and the compound is obtained from 5-chloroacridine and Na_2Se . 10-Alkylselenoacridones are obtained from acridones- POCl_3 and K_2SeSO_3 whereby much Se is also pptd. KCNSe does not appear suitable. 10-Methyl-, m.p. 263°, and 10-ethyl-, m.p. 218°, -thioacridone and 10-methyl-, m.p. 259°, 10-ethyl-, m.p. 242—243°, and 10-phenyl-selenoacridone, m.p. 228°, are described.

H. W.

Pyridionaphthalones. A. TAURINS (J. pr. Chem., 1939, [ii], 153, 177—188).—1:8- $\text{C}_{10}\text{H}_8(\text{CO})_2\text{O}$ (I), ZnCl_2 (0.7 mol.), and 2-methylpyridine at 230° slowly give 2-2'-pyridylperinaphthindane-1:3-dione, m.p. 269° (yield 23.2%) [mol. compound (2:1) with (I), m.p. 243—245°; hydrochloride, m.p. 269°; Na (II) and Ag salts]. Addition of Br in CHCl_3 to (II) in the



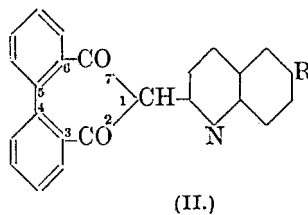
same solvent affords the Br_1 -derivative (III), m.p. 140° (decomp.), from which Br is readily removed by aq. NaOH and which adds 2 Br to give a

yellow unstable tribromide (two Br united co-ordinatively to N), which loses 2 Br when its solution in CHCl_3 is boiled. 2:6-Dimethylpyridine, (I), and ZnCl_2 at 200—230° give 2-6'-methyl-2'-pyridylperinaphthindane-1:3-dione, m.p. 239—240° (hydrochloride; Na and Ag salts; Br_1 -, m.p. 135—137°, and Br_3 -compounds, m.p. 205—206° after softening at 150—151°). 2:4-Dimethylpyridine at 230—240° affords 2-4'-methyl-2'-pyridylperinaphthindane-1:3-dione, m.p. 256—257° (hydrochloride; Na and Ag salts; Br_1 -, m.p. 145—147°, and Br_3 -, m.p. 150—160° (decomp.), -derivatives). 2:4:6-Trimethylpyridine at 230° yields 4':6'-dimethyl-2'-pyridylperinaphthindane-1:3-dione, m.p. 296—298° after incipient decomp. at 270° [hydrochloride, m.p. 290° (decomp.); Na salt; Br_1 -, m.p. 210° after incipient decomp. at 160°, and Br_3 -compounds].

H. W.

Condensation of diphenic anhydride with methylpyridines and methylquinolines. A. TAURINS (J. pr. Chem., 1939, [ii], 153, 189—199).—

Diphenic anhydride (I) is converted by 2-methylquinoline, best in the presence of a small proportion of ZnCl_2 at 170—180°, into 1-2'-quinolyl-3:4:5:6-dibenzocycloheptadiene-2:7-dione (quinodiphenone) [(II), R = H], m.p. 231° (phenylhydrazone, m.p. 184°; 2:4-dinitrophenylhydrazone, m.p. ~300°), oxidised by 30% H_2O_2 in



AcOH to diphenic and quinoline-2-carboxylic acid. 2:6-Dimethylquinoline at 200° similarly yields 1:6'-methyl-2'-quinolyl-3:4:5:6-dibenzocycloheptadiene-2:7-dione (toluquinodiphenone), m.p. 262°. 2-Methylpyridine, (I), and ZnCl_2 react slowly at 170—240° giving 1-2'-pyridyl-3:4:5:6-dibenzocycloheptadiene-2:7-dione (2-pyridodiphenone), m.p. 200°, in 25% yield. 1-6'-Methyl-, m.p. 195°, 1-4'-methyl-, m.p.

243—244°, and 1-4':6'-dimethyl-, m.p. 220°, -2'-pyridyl-3:4:5:6-dibenzocycloheptadiene-2:7-dione are described.

H. W.

N-Menthyl-substituted amides. A. R. DAY and C. F. KELLY (J. Org. Chem., 1939, 4, 101—102; cf. Read and Storey, A., 1931, 229).—The following N-menthyl derivatives are prepared, from equiv. amounts of free base and acyl chloride in C_6H_6 , in yields of 80—90%: - α -, m.p. 138.5°, and - β -bromopropionamide, m.p. 86°; - α -bromo-n-, m.p. 150°, and -iso-butylamide, m.p. 94.5°; - α -bromo-n-, m.p. 166°, and -iso-valeramide, m.p. 184—184.5°; -p-nitro-, m.p. 172.5—173°, reduced by Fe-EtOH-HCl at 15—20° to -p-amino-benzamide, m.p. 190.5—191°. 5-(α -isopropyl-5-methylpentamethylene)hydantoin, m.p. 223—225° (optically inactive), is obtained from l-menthone and KCN-(NH_4)₂CO₃-aq. EtOH at 60°. Physiological tests show the compounds to be of little val. as hypnotics.

A. T. P.

Optically active isoamarines. I. LIFSCHITZ and J. G. Bos (Rec. trav. chim., 1939, 58, 638—642; cf. Snape, J.C.S., 1900, 77, 778).—isoAmarine gives d-tartrates, m.p. 196°, [α]_D +123.7° (all in 96% EtOH), and m.p. 207°, [α]_D -107.4°, and thence the d-, m.p. 180°, [α]_D +46.3° (+140.1° in 0.1N-HCl), and l-base, m.p. 180°, [α]_D -46.9°. [α] is also given for 10 other λ .

A. T. P.

Reactions and formation of salts of 1-phenyl-3-methyl-5-pyrazolone and of oximino- ψ -thiohydantoin.—See A., 1939, I, 429.

New group in the diketopyrazolidine series. B. HEFNER and A. SIMONBERG (Bull. Soc. chim., 1939, [v], 6, 1069—1076).—CH₃(CO·NH·NH₂)₂ and aq. NaOH, then just acid with AcOH, give malonyldihydrazidoacetic acid, " α -hydrazomalonic acid," NH₂·NH·CO·CH₂·CO·NH·NH·CH₂·CO₂H, decomp. ~230°, converted by aq. NaNO₂-AcOH at <10° into the Na salt (+4H₂O) (I) of 4-oximino-1:2-oximinomalonyl-3-keto-2:3-dihydro-5-pyrazolone [4-oximino-1:2-oximinomalonyl-3:5-diketopyrazolidine] (" ψ -urazolic acid"). Its K (+0.5H₂O), Ag, Hg, Pb, Cu, Ba, Ca, and Mg salts are similar to the salts of violuric acid. When heated (I) becomes red, then violet. (I) and HNO₃ (d 1.4) at <20°, then 95°, give the Na salt (+1.5H₂O) of 4-nitro-1:2-nitromalonyl-3-keto-2:3-dihydro-5-pyrazolone (" ψ -diliturazolic acid") (Ag salt), decomp. violently by heat. (I) and Na₂S₂O₄ at 90° give the Na salt of thionurazolic acid [Na 4-amino-1:2-aminomalonyl-3:5-diketopyrazolidine-N-sulphoxylate],

NH₂·CH<CO·N·CO>CH·NH·SO₂Na, converted by dissolution in aq. NaOH and acidifying with HCl into 4-amino-1:2-aminomalonyl-3-keto-2:3-dihydro-5-pyrazolone [4-amino-1:2-aminomalonyl-3:5-diketopyrazolidine] (" ψ -uramilazole"). The latter and KCN give the K salt of ψ -ureidazolic acid,

NH₂·CO·NH·CH<CO·N·CO>CH·NH·CO·NH₂ (acid, +0.5H₂O), which at 150° affords the K salt, OK·C<NH·C·CO·N·CO·C·NH>C·OK, +2.25H₂O, of ureidazolic acid.

A. T. P.

Synthesis of 2-ethylglyoxaline derivatives. **Synthesis of 4:5-diaminomethyl-2-ethylglyoxaline.** Y. TAMAMUSHI (J. Pharm. Soc. Japan, 1938, 58, 1—3).—Et₂ 2-ethylglyoxaline-4:5-dicarboxylate, m.p. 94° [hydrochloride (I), m.p. 175°], is obtained by esterifying the acid with HCl-EtOH. 28% NH₃ transforms (I) into 2-ethylglyoxaline-4:5-dicarboxylamide, m.p. 258°, dehydrated by POCl₃ at 90—100° to the dinitrile, m.p. 185°, which is reduced by Na and EtOH or catalytically (Pd-C) to 4:5-diaminomethyl-2-ethylglyoxaline (trihydrochloride, m.p. 262°).

H. W.

Vitamin research. T. B. JOHNSON and M. M. ENDICOTT (Science, 1939, 89, 297—298).—2:4-dihydroxy-5-methyl-6-chloromethylpyrimidine is stable towards conc. HCl at 125—130°, but 2:4-dihydroxy-6-methyl-5-chloromethylpyrimidine is unstable when digested with H₂O or alcohol and is converted quantitatively into bis-(2:4-dihydroxy-6-methyl-5-pyrimidyl)methane by HCl.

L. S. T.

Diketotriazine ethers. E. CATTELAÏN (Compt. rend., 1939, 208, 1656—1658; cf. Bougault, A., 1914, i, 1004).—Diethers of sulphonyltriazines when hydrolysed with HCl-EtOH give RSH and an N-monoether (I) [different from that (II) described by Bougault], also obtained by interaction of R·CO·CO₂H and NH₂·NR·CO·NH₂. Etherification of (I) gives NN-diethers identical with those obtained by Bougault by etherifying (II). The following are prepared: 3:5-diketo-6-benzyl-2-methyl-, m.p. 137°, -6-benzyl-2-ethyl-, m.p. 103°, and -2:6-dibenzyl-1:2:4-triazine, m.p. 113°.

J. L. D.

Benzporphins. VI. Catalytic hydrogenation of o-cyanoacetophenone. Synthesis of a dye of the benzporphin series. J. H. HELBERGER and A. VON REBAY (Annalen, 1939, 539, 187—206; cf. A., 1939, II, 128).—o-CN·C₆H₄·COMe and H₂-Pd-black in MeOH-HBr (d 1.49) slowly give 3-methylphthalimidine (I), o-C₆H₄<CO>NH, probably by way of

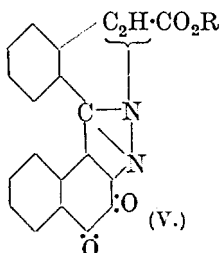
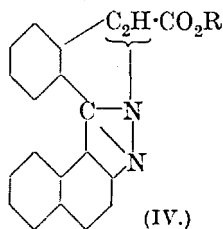
o-COMe·C₆H₄·CH·NH and o-C₆H₄<CH>N (II).

H₂-Raney Ni in Et₂O at 70—75°/50 atm. gives only a little (I), ~45% of a yellow product (III), C₁₈H₁₆N₂, 0.5H₂O and anhyd., m.p. ~120° (decomp.), ~10% of a yellow product (IV), C₁₈H₁₆ON₂, m.p. 190—195° (decomp.), and traces of a violet-red product, C₁₈H₁₆N₂, m.p. 237°; at >100° some tetrabenzporphyrin (V) is also formed. Atm. oxidation of (III) to (IV) occurs very readily and (IV) is probably formed as secondary product from (III). Conc. HNO₃ oxidises (IV) to o-C₆H₄(CO)₂O and o-C₆H₄(CO)₂NH. The structure CH<C₆H₄>CH·CH₂·C<C₆H₄>C·CH₂ is suggested for (III), derived from 2 mols. of (II), and is supported by the following reactions. At 250° (III) gives (V), but (IV) gives also another pigment. Pyrolysis of (IV), best in 1-C₁₀H₇Cl at 200°, gives isoelectrobenzporphyrin (VI), C₃₆H₂₂N₄, violet, absorption max. at 673, 631, 595, and 440 m μ . in C₅H₅N, which gives Zn, Fe⁺⁺ (+2C₅H₅N), and Cu derivatives (absorption max. listed); in 1-C₁₀H₇Cl at 200° in presence of air, (III) gives mainly (V) with some (VI). (VI) may be a reduced form of (V).

R. S. C.

Pyrido(1':2':1:2)benziminazoles and allied compounds (cyclic 1:3-diazalines). II. (SIR) G. T. MORGAN and J. STEWART (J.C.S., 1939, 1057—1066; cf. A., 1938, II, 459).—*N*-2':4'-Dinitrophenyl-2-aminopyridine [from 2-aminopyridine and 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ in boiling xylene, together with a by-product, m.p. $>280^\circ$] when heated in C_{10}H_8 or Ph_2 at $300\text{--}310^\circ$ yields 1:2-pyrido-7-nitro-4:5-benz-1:3-diazaline, reduced (H_2 , PtO_2 under pressure) to the NH_2 -compound, converted by diazotisation into 1:2-pyrido-4:5-benz-1:3-diazaline. The last three compounds are identical with those obtained (*loc. cit.*) by eliminating NO_2 from the $(\text{NO}_2)_2$ -compound. Similarly quinoline in boiling PhNO_2 yields *N*-2':4'-dinitrophenyl-2-aminoquinoline, m.p. 221° , 1:2-quinolo-7-nitro- and -amino-4:5-benz-1:3-diazaline, and quinolobenzdiazaline, the last three identical with the products obtained (*loc. cit.*) from the $(\text{NO}_2)_2$ -compound. *iso*Quinoline (in boiling xylene) yields *N*-2':4'-dinitrophenyl-1-aminoisoquinoline, m.p. $230\text{--}231^\circ$, 1:2(2':1')-isoquinolo-7-nitro-, m.p. $271\text{--}272^\circ$, and -amino-4:5-benz-1:3-diazaline, m.p. $266\text{--}267^\circ$, and isoquinolobenzdiazaline, m.p. 129° , the last three identical with the products obtained from the $(\text{NO}_2)_2$ -via the nitro-amino-compound. *N*-2':4'-Dinitro-1'-naphthyl-2-aminopyridine in boiling PhNO_2 yields 1:2-pyrido-7-nitro-8:9-benzo-4:5-benz-1:3-diazaline, m.p. $240\text{--}241^\circ$, reduced to the NH_2 -compound, m.p. $238\text{--}239^\circ$, and further to the 1:2-tetrahydro-pyrido-7-aminobenzobenzdiazaline, m.p. $228\text{--}230^\circ$. The last two on diazotisation yield pyrido-, m.p. 187° , and tetrahydropyrido-benzobenzdiazaline, m.p. $158\text{--}159^\circ$. By similar methods quinoline and isoquinoline yield *N*-2':4'-dinitro-1'-naphthyl-2-aminoquinoline, m.p. 262° , and -1-aminoisoquinoline, m.p. 232° ; 1:2-quinolo-, m.p. $>280^\circ$, and 1:2(2':1')-isoquinolo-7-nitro-8:9-benzo-4:5-benz-1:3-diazaline, m.p. $>280^\circ$; 1:2-quinolo-, m.p. $244\text{--}245^\circ$, and 1:2(2':1')-isoquinolo-7-aminobenzobenzdiazaline, m.p. $252\text{--}253^\circ$; and 1:2-quinolo-, m.p. 166° , and 1:2(2':1')-isoquinolobenzobenzdiazaline, m.p. 184° (shrinking at 170°). A. LI.

Anomalous decomposition of the tetrazo-derivative of 2:2'-diamino-1:1'-dinaphthyl. V. Oxidation of *cis*-o-naphtho-1':2':4:5-pyrazolyl-3-cinnamic acid. A. CORBELLINI, F. CAPUCCI, and G. TOMMASINI (Gazzetta, 1939, 69, 137—150).—The Me (I) and Et (II) esters of *cis*-o-naphtho-1':2':4:5-pyrazolyl-3-cinnamic acid (III) (A., 1931, 966) with $\text{Pb}(\text{OAc})_4\text{-AcOH}$ give respectively the *Me*, m.p. $238\text{--}239^\circ$, and *Et*, m.p. $237\text{--}238^\circ$, esters (IV) of the acid $\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_2$. These are also and better



obtained (cf. Corbellini *et al.*, A., 1939, II, 88) from the corresponding acid chloride prepared from (III)

and SOCl_2 . With $\text{CrO}_3\text{-AcOH}$ (6 hr.), (I) gives the quinone (V) ($\text{R} = \text{Me}$), m.p. $335\text{--}338^\circ$ (decomp. from 310°) [*mono-oxime*, m.p. $240\text{--}246^\circ$ (decomp.)]; *phenazine* derivative, m.p. 327° , also obtained by oxidising (IV) ($\text{CrO}_3\text{-AcOH}$). With aq. KOH-EtOH , (V) ($\text{R} = \text{Me}$) gives, after acidification, products, m.p. $250\text{--}256^\circ$, and 310° (impure), which with $\text{KMnO}_4\text{-Na}_2\text{CO}_3$ give $(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{O})_2$. Similarly (II) gives the quinone (V) ($\text{R} = \text{Et}$), m.p. 327° (decomp. from 320°) [*phenazine* derivative, m.p. 281° (decomp. from 250°)], also obtained from (IV) ($\text{R} = \text{Et}$). Reduction (Zn-AcOH) of (V) ($\text{R} = \text{Me}$), followed by oxidation in air, gives *Me cis*-o-3':4'-diketonaphtho-1':2':4:5-pyrazolyl-3-cinnamate (VI), m.p. $290\text{--}292^\circ$ (decomp. from 260°) [*phenazine* derivative, m.p. 292° (decomp. from 288°)], also obtained from (I) and $\text{CrO}_3\text{-AcOH}$ under somewhat different conditions from (V) [which is insol. in boiling AcOH , that dissolves (VI)]. With $\text{Zn-Ac}_2\text{O}$, (V) ($\text{R} = \text{Me}$) gives a diacetyldihydro-compound, m.p. $205\text{--}206^\circ$, also obtained from (VI). Similarly, reduction of (V) ($\text{R} = \text{Et}$) and atm. oxidation give the *Et* (VII), m.p. 312° (decomp. from 260°), analogue of (V); (VII) gives a *phenazine*, m.p. $265\cdot5^\circ$ (decomp. from 262°), and a diacetyldihydro-compound, m.p. $203\text{--}205\cdot5^\circ$. $\text{CrO}_3\text{-AcOH}$ [but not $\text{Pb}(\text{OAc})_4$] converts (VI) and (VII) into (V) ($\text{R} = \text{Me}$ and Et respectively). E. W. W.

Quinoxalines.—See B., 1939, 778.

Methylated and methoxylated 10:10'-dimethyldiacridenes and 10:10'-dimethyldiacridylium salts. K. GLEU and S. NITZSCHE (J. pr. Chem., 1939, [ii], 153, 233—241).—Reduction of substituted 10-methylacridones (I) to the corresponding diacridenes (cf. A., 1935, 1254) cannot be effected with Zn dust in boiling AcOH and only unsatisfactorily with Zn and HCl-EtOH . A general method consists in the conversion of (I) into additive compounds with POCl_3 which are readily reduced by Zn dust in COMe_2 or by aq. $\text{Cr}(\text{OAc})_2$. The diacridenes are markedly fluorescent and show strong chemiluminescence when their solutions in cyclohexanone, preferably in presence of EtOH , are brought in contact with air; addition of a little H_2O_2 and passage of NH_3 over the surface of the solution greatly increases the effect. Magnetic measurements show that the diacridenes are not biradicals. Oxidation of substituted diacridenes to diacridylium salts is best achieved with boiling, dil. HNO_3 , whereby the nitrates are obtained. The 1:1' derivatives show little, if any, chemiluminescence; this is less intense with the 2:2' derivatives than with the parent substance, and with the 4:4'-(OMe) $_2$ -compound the colour is very dependent on the concn. The behaviour contributes little to the knowledge of the mechanism of chemiluminescence. The following diacridenes are described: 1:1':10:10', m.p. 410° , 2:2':10:10', m.p. 330° , 3:3':10:10', m.p. 354° , and 4:4':10:10'-tetramethyl-, m.p. 355° ; 1:1', m.p. 375° , 2:2', m.p. 294° , 3:3', m.p. 322° , and 4:4'-dimethoxy-10:10'-dimethyl-, m.p. 297° . The following diacridylium salts are new: 1:1':10:10'-tetramethyl-borofluoride, 2:2':10:10'-tetramethyl-*H* nitrate, $\text{C}_{30}\text{H}_{26}\text{N}_2(\text{NO}_3)_2\cdot 2\text{HNO}_3$, 3:3':10:10', $\text{C}_{30}\text{H}_{26}\text{N}_2(\text{NO}_3)_2\cdot \text{HNO}_3\cdot 3\text{H}_2\text{O}$, and 4:4':10:10'-tetramethyl-*H* nitrate, $\text{C}_{30}\text{H}_{26}\text{N}_2(\text{NO}_3)_2\cdot 2\text{HNO}_3$, 1:1'-di-

methoxy-10 : 10'-dimethyl- borofluoride, 2 : 2'-, $C_{30}H_{26}O_2N_2(NO_3)_2 \cdot HNO_3 \cdot 2H_2O$, 3 : 3'-, $C_{30}H_{26}O_2N_2(NO_3)_2 \cdot 2H_2O$, and 4 : 4'-*dimethoxy-10 : 10'-dimethyl- nitrate*, $C_{30}H_{26}O_2N_2(NO_3)_2 \cdot 3H_2O$. H. W.

Xanthopterin. C. SCHÖPF and A. KOTTLER (Annalen, 1939, 539, 128—155; cf. A., 1936, 882, 1260, 1404; 1938, II, 66).—Prep. of pure β -xanthopterin (I) and crude chrysopterin and guanopterin from *Catopsilia rurina* (male) is detailed. Aq. $NaClO_3$ -HCl at 100° oxidises (I), $C_{19}H_{18}O_6N_{16}$, to $H_2C_2O_4$ (3.65), $CHO \cdot CO_2H$ (0.74), $NH_2C(NH_2)_2$ (0.49), $CO(NH_2)_2$ (0.35), NH_3 (6.85), and CO_2 (7.25 mols.). The 4.4 mols. of C_2 acids proves the presence of two C_2 chains attached to the three pyrimidine nuclei. The symmetrical structure of three pyrimidine rings, each carrying a C_2 chain and attached to the last C as in $CHPh_3$, is suggested. $NaClO_3$ -HCl and (I) at 80° give 1.32 mols. of $NH_2C(NH) \cdot NH \cdot CO \cdot CO_2H$ (II) [hydrolysed by acid to $H_2C_2O_4$ and $NH_2C(NH_2)_2$ and by alkali to $H_2C_2O_4$, NH_3 , and $CO(NH_2)_2$] with $H_2C_2O_4$ (2.3), $NH_2C(NH_2)_2$ (0.38), NH_3 (5.65), and CO_2 (3.14 mols.); 2 : 4 : 5-triamino-6-hydroxypyrimidine (III) under similar conditions yields 46% of (II), and the 1.32 mols. obtained from (I) is thus equiv. to 2.87 mols. There are thus three 2-amino-pyrimidine rings in (I). Aq. $NaNO_2$ liberates all the N from (I) as N_2 at 80° and all the C as CO_2 at 100°; at 60° decomp. is only partial, but definite products are not obtained; (III) is similarly decomposed. Addition of (I) and then of ice or dil. AcOH to $NO \cdot HSO_4$ in conc. H_2SO_4 gives (II) (1.42), $NH_2C(NH_2)_2$ (0.81), and $CHO \cdot CO_2H$ (0.64 mol.). O_3 oxidises (I) in $N \cdot NaOH$ to (II) (2.02), $H_2C_2O_4$ (1.89 mols.), and $NH_2C(NH_2)_2$; (III) gives similarly $H_2C_2O_4$ and $NH_2C(NH_2)_2$, but the colour changes are different. Other reactions of (I) are briefly referred to.

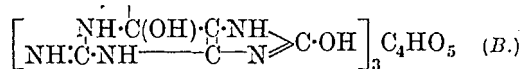
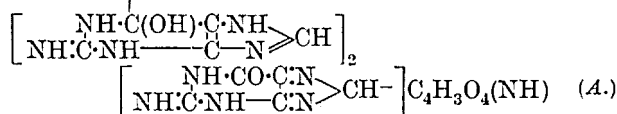
R. S. C.

Hydrolysis of pterins by acids. C. SCHÖPF, E. BECKER, and R. REICHERT (Annalen, 1939, 539, 156—168).—Glycine (I) is determined (83—85% recovered) as hippuric acid. Uric acid, guanine, and 2 : 4 : 5-triamino-6-hydroxypyrimidine and 15% HCl at 200° or 15% HCl and $ZnCl_2$ at 160° give 61—64% of (I). Taking this as a factor, xanthopterin and erythropterin give 2 mols. and 1 mol., respectively, of (I); after reduction by Zn dust and HCO_2H , each gives 3 mols.; they thus contain 1 and 2 rings, respectively, as $NH_2C \begin{smallmatrix} \diagup NH \cdot CO \cdot C \cdot N \diagdown \\ \diagdown NH \diagup \end{smallmatrix} C \cdot N$, which, when reduced, give $NH_2C \begin{smallmatrix} \diagup NH \cdot CO \cdot C \cdot NH \diagdown \\ \diagdown NH \diagup \end{smallmatrix} C \cdot NH$. Guanopterin gives 4 equivs. of (I) and probably contains a chain, $CO \cdot NH \cdot CH_2 \cdot CO \cdot NH$, attached to one ring.

R. S. C.

Wing pigments of butterflies. IV. Relations between xanthopterin and leucopterin. H. WIELAND and R. PURRMANN (Annalen, 1939, 539, 179—187; cf. A., 1937, II, 392).—Xanthopterin (I) gives an additive compound, $C_{19}H_{20}O_7N_{16} \cdot 3H_2SO_3$, decomposed into (I) by alkali or hot dil. acid. With H_2O_2 it gives a similar compound, (I). $3H_2O_2$, decomp. >100°, reverting to (I) in cold, aq. alkali or hot H_2O and converted by further treatment at room temp. into *iminoleucopterin*, $C_{19}H_{20}O_{10}N_{16}$, which with

HNO_2 exchanges 4 NH for 4 O and gives de-imino-leucopterin. H_2O_2 at 100° gives melanuric acid.



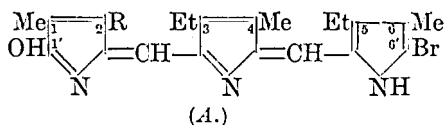
(A) and (B) are probable formulae for (I) and leucopterin, respectively, although the formation of the Ba salt is obscure.

R. S. C.

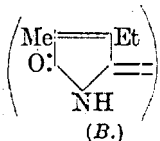
Bile pigments. XXIV. Hydroxynitrovinylpyrromethenes and urobilinoid pigments. H. FISCHER and H. REINECKE (Z. physiol. Chem., 1939, 258, 243—254).—2 : 4-Dimethyl-3-nitrovinylpyrrole (I) (A., 1928, 902) is converted by HCN in $CHCl_3$ followed by H_2O into 2 : 4-dimethyl-3-nitrovinylpyrrole-5-aldehyde, m.p. 242°. Et 2 : 4-dimethyl-3-nitrovinylpyrrole-5-carboxylate is transformed by SO_2Cl_2 into Et 4-methyl-2-trichloromethyl-3- $\alpha\beta$ -dichloro- β -nitroethylpyrrole-5-carboxylate, m.p. 148°, in modest yield. (I) condenses with 3 : 3'-dimethyl-5 : 5'-dibromomethyl-4 : 4'-diethylpyrromethene hydrobromide to 1' : 8' : 2 : 4 : 5 : 7-hexamethyl-3 : 6-diethyl-1 : 8-dinitrovinylbilien(4' ms) hydrobromide, m.p. >300°, which gives the Gmelin reaction but does not show a green fluorescence with $Zn(OAc)_2$ in EtOH; the free base rapidly becomes dehydrogenated. 3 : 3'-Dimethyl-5 : 5'-dibromomethyl-4-ethylpyrromethene-4'-propionic acid hydrobromide and (I) give Me 1' : 8' : 2 : 4 : 5 : 7-hexamethyl-3-ethyl-1 : 8-dinitrovinylbilien(4' ms)-6-propionate hydrobromide, m.p. >300°, whilst formyllopsopyrrolecarboxylic acid and (I) afford 3 : 3' : 5'-trimethyl-4-nitrovinylpyrromethene-4'-propionic acid hydrobromide, which with $Zn(OAc)_2$ in EtOH gives a red colour and an involved spectrum in the green. Bromo-opsopyrrolecarboxyaldehyde and (I) yield 5-bromo-3 : 3' : 5'-trimethyl-4'-nitrovinylpyrromethene-4-propionic acid hydrobromide (free base, m.p. 200°), converted by KOAc in boiling AcOH into 5-hydroxy-3 : 3' : 5'-trimethyl-4-nitrovinylpyrromethene-4-propionic acid, m.p. 275° (decomp.). 5-Bromo-3' : 4 : 5'-trimethyl-3-ethyl-4'-nitrovinylpyrromethene hydrobromide, no distinct m.p., is similarly transformed into 5-hydroxy-3' : 4 : 5'-trimethyl-3-ethyl-4'-nitrovinylpyrromethene, m.p. 306°. 5-Bromo-3-methyl-4-ethylpyrrole-2-aldehyde is condensed with (I) in MeOH-HBr to 5-bromo-3 : 3' : 5'-trimethyl-4-ethyl-4'-nitrovinylpyrromethene hydrobromide, whence is derived 5-hydroxy-3' : 3 : 5'-trimethyl-4-ethyl-4'-nitrovinylpyrromethene, m.p. 315°. *Ætiomesoglaucobilin*, HBr, and Br in AcOH give a hydrobromide *perbromide* which gives a green solution with red fluorescence with $Zn(OAc)_2$ in EtOH; it is transformed by warm $COMe_2$ into *ætiomesoglaucobilin hydrobromide*, m.p. 245°. Aminoantipyrine and ($\cdot CHAc \cdot CO_2Et$)₂ in AcOH at 100° yield 3' : 4-dicarbethoxy-2' : 5'-dimethyl-1'-pyrryl-1-phenyl-2 : 3-dimethylpyrazolone, m.p. 145°, hydrolysed (KOH-EtOH at 100°) to the free acid, m.p. 256° (decomp.), which is decarboxylated at ~260° to 2' : 5'-dimethyl-1'-pyrryl-1-phenyl-2 : 3-dimethylpyrazolone, m.p. 178°.

H. W.

Bile pigments. XXV. Tripyrrenes. H. FISCHER and H. REINECKE (Z. physiol. Chem., 1939, 259, 83—96).—5-Bromo-4-methyl-3-ethylpyrrole-2-aldehyde (I) (2 mols.) with β -2-hydroxy-3-methyl-4-pyrrolylpropionic [hydroxyopopyrrolicarboxylic] acid (II) (1 mol.) in MeOH + 48% HBr for 24 hr. gives 6'-bromo-1'-hydroxy-1 : 4 : 6-trimethyl-3 : 5-diethyl-2- β -carbomethoxyethyltripyrrene (A, R = [CH₂]₂·CO₂Me; double linkings assigned arbitrarily), m.p. 200°, apparently



formed by further condensation (and esterification) of the intermediate 5-bromo-5'-hydroxy-4 : 4'-dimethyl-3-ethyl-3'- β -carboxyethylpyrromethene (labile Br) with (I). Similarly, β -5-bromo-2-aldehydo-3-methyl-4-pyrrolylpropionic acid (III) and (II) afford 6'-bromo-1'-hydroxy-1 : 3 : 5-trimethyl-2 : 4 : 6-tri- β -carbomethoxyethyltripyrrene, m.p. 185°, also obtained (m.p. 187°) from (III) and coproneoxanthobilirubic acid. Neoxanthobilirubic acid (IV) and (I) in boiling MeOH-48% HBr give 6'-bromo-1'-hydroxy-1 : 3 : 6-trimethyl-2 : 5-diethyl-4- β -carbomethoxyethyltripyrrene, m.p. 207°, whilst the isomeric 1 : 3 : 5-trimethyl-2 : 6-diethyl-derivative, m.p. 197°, is obtained from (IV) and 5-bromo-3-methyl-4-ethylpyrrole-2-aldehyde (V). 6'-Bromo-1'-hydroxy-1 : 3 : 5-trimethyl-2-ethyl-4 : 6-di- β -carbomethoxyethyltripyrrene, m.p. 184°, is formed from (III) and (IV) and probably from (III) and (VI) (below). isoNeoxanthobilirubic acid is converted by prolonged treatment with MeOH-48% HBr into a tripyrrene, m.p. 125°, and the corresponding glaucobilin, m.p. 232°, separated by chromatographic adsorption (Al₂O₃); the acid with (I), (V), and (III) gives 6'-bromo-1'-hydroxy-2 : 3 : 6-trimethyl-1 : 5-diethyl-4- β -carbomethoxyethyl-, m.p. 180°, -2 : 3 : 5-trimethyl-1 : 6-diethyl-4- β -carbomethoxyethyl-, m.p. 172°, and -2 : 3 : 5-trimethyl-1-ethyl-4 : 6-di- β -carbomethoxyethyl-tripyrrene, m.p. 130°, respectively. 6'-Bromo-1'-hydroxy-1 : 3 : 6-trimethyl-2 : 4 : 5-triethyltripyrrene, m.p. 218°, is obtained from (I) and α -ioneoxanthobilirubic acid. Oxidation (H₂O₂) of opopyrrole in C₅H₅N at 50—60° affords hydroxyopopyrrole (VI), m.p. 62° (removed by distillation), and the diketone (B), m.p. >300°. PhN₂Cl with (VI) and



(II) in aq. MeOH gives di(benzene-azo)-derivatives (hydrochlorides, m.p. 170° and 206°, respectively). Vinyl-neoxanthobilirubic acid with (I) and (III) in MeOH-HBr yields 6'-bromo-1'-hydroxy-1 : 3 : 6-trimethyl-5-ethyl-4- β -carbomethoxyethyl- (VII), m.p. 191°, and -1 : 3 : 5-trimethyl-4 : 6-di- β -carbomethoxyethyl- (VIII), m.p. 156°, -2-vinyltripyrrene, respectively. The AcOH mother-liquors from the bromination of 5-aldehydo-3-methyl-4-ethylpyrrole-2-carboxylic acid, when kept for 24 hr., contain a glaucobilin and (probably) 6'-bromo-1'-hydroxy-1 : 4 : 6-trimethyl-2 : 3 : 5-triethyltripyrrene, m.p. 216°, separable by chromatographic adsorption (Al₂O₃).

The tripyrrenes are sensitive reagents for Zn (even in presence of Al), giving blue colorations with red

fluorescence with aq. Zn(OAc)₂ (1 mg. per l.); (VII) and (VIII) are most useful. H. B.

Bile pigments. XXVI. Stercobilin. H. FISCHER and H. LIBOWITZKY (Z. physiol. Chem., 1939, 258, 255—277).—Acidification of faeces with tartaric acid followed by extraction with EtOH-Et₂O and adsorption with Al₂O₃ gives the chromogens (I), from which a bilirubin (II) and stercobilin hydrochloride (III) are isolated. (II), m.p. >360°, is C₃₃H₃₆O₆N₄. It is optically inactive. It is hydrogenated (colloidal Pd) to mesobilirubin. It is not oxidised by HNO₃ to methylethylmaleimide. (III) contains CHCl₃ which is difficult to remove completely; this is best effected by boiling with COMe₂ and CH₂(OMe)₂, thereby giving stercobilin (IV), C₃₃H₄₆O₆N₄, m.p. 236° (corr.), [α]_D²⁰₋₇₂₀ +256°, -254°, +260°, -322°, -139° and +32.8° in HCO₂H, AcOH, HCO₂H + AcOH (1 : 1), CHCl₃, 0.5N-NaOH, and 38% HCl respectively. (IV) causes quant. reduction of AgOAc (2—8 mols.) to Ag, giving dark brown pigments which could not be examined polarimetrically. Dehydrogenation with Pd and maleic anhydride is unsuccessful and Pb(OAc)₄ in AcOH gives non-cryst. products. Ascorbic acid and atm. O₂ in C₅H₅N appear to be without action in 24 hr. Molten resorcinol causes chiefly the formation of colourless acids with an intense, positive Ehrlich reaction for aldehydes. They are readily autoxidised and could not be obtained cryst. Optical activity could not be detected. Reduction with AcOH-HI-PH₄I does not yield basic components in 2 hr. (IV) is converted quantitatively into non-cryst., autoxidisable, optically active acids with intensely positive Ehrlich reaction. After 24 hr. very small amounts of basic components are present but the acids remain the chief products. Apparently (IV) gives only dinuclear products and mononuclear substances have not yet been obtained. Oxidation of (IV) with CrO₃ and H₂SO₄ gives a comparatively small, non-cryst. basic fraction which is strongly dextrorotatory in EtOH; the main product is a levorotatory acidic oil containing crystals of (·CH₂·CO₂H)₂. The intermediate production of pentuopent is not observed. Stercobilinogen (V), obtained by reduction with Na-Hg or catalytically (colloidal Pd in NaOH or PtO₂ in AcOH), is non-cryst. and optically inactive. Further purification and examination of (I) leads to the conclusion that the "urobilinogen" of the faeces is a mixture of (V) and mesobilirubinogen (VI). Other isolated products are a compound, m.p. 192° after softening at 160°, with positive Cu reaction, which does not show the cryst. form of (VI), and another substance which exhibits the form but could not be isolated from the oily mother-liquors. The amount of methylethylmaleimide obtained shows that the amount of (V) greatly exceeds that of (VI). Other chromogens do not appear to be present. The parent of (V) and (VI) in faeces is probably bilirubin. H. W.

Mesobilifuscin, a degradation product of hæm or hæmatin. I. Constitution and partial synthesis. W. SIEDEL and H. MÜLLER (Z. physiol. Chem., 1939, 259, 113—136).—Mesobilifuscin (I) (following abstract) is identical with the "substance II" of Fischer (A., 1911, i, 803, 1005; 1912, i, 575)

obtained during reduction (5% Na-Hg, 0.1N-NaOH) of crude bilirubin. The crude (I) thus obtained is purified by esterification (MeOH-HCl), subsequent treatment with FeCl_3 (whereby admixed urobilin and mesobilirubinogen are oxidised to bilirubinoids), and chromatographic adsorption (Brockmann's Al_2O_3), giving the non-cryst. Me ester (II), $\text{C}_{17}\text{H}_{22}\text{O}_4\text{N}_2$, m.p. 172—176°. Hydrolysis (MeOH-KOH) then affords (I), m.p. >340°, which is shown to be (probably) 5 : 5'-dihydroxy-3 : 4'-dimethyl-3'-ethyl- (III) or -3 : 3'-dimethyl-4'-ethyl-4- β -carboxyethylpyrromethene (IV) or a mixture of both. Fusion of (II), which contains 3 active H, with $m\text{-C}_6\text{H}_4(\text{OH})_2$ results only in hydrolysis to (I). Oxidation (fuming HNO_3) of (II) gives methylethynaleimide and hæmatic acid; reduction by Zn dust-AcOH affords an unstable compound [readily oxidised to (II)], whilst AcOH-HI (*d* 1.94) gives opsopyrrolecarboxylic acid but no cryptopyrrole or cryptopyrrolecarboxylic or bilirubic acid. Oxidation [$\text{Pb}(\text{OAc})_4$ -AcOH] of mesobilirubinogen IX α yields (I); other compounds, including coproporphyrin III, are formed and separated as Me esters by chromatography. Similar oxidation of mesobilirubinogen XIII α , urobilin XIII α , mesobilirubin XIII α , and glaucobilin XIII α also gives (I) or an isomeride; the Me esters have m.p. 149°, —, 145°, and 150—151° (all corr.), respectively. Me neoxanthobilirubate (V) is similarly oxidised to ketomesobilifuscin I Me ester [5 : 5'-dihydroxy-3 : 4'-dimethyl-3'-ethyl-4- β -carbomethoxyethyl-2 : 2'-dipyrryl ketone], m.p. 155—156° (corr.). Successive oxidation, reduction (Na-Hg), and treatment with MeOH-HCl convert neoxanthobilirubic acid into mesobilifuscin I Me ester [= Me ester of (III)], which has the properties of (II). Ketomesobilifuscin II Me ester [5 : 5'-dihydroxy-3 : 3'-dimethyl-4'-ethyl-4- β -carbomethoxyethyl-2 : 2'-dipyrryl ketone], m.p. 188° (corr.), and mesobilifuscin II Me ester [= Me ester of (IV)], m.p. 170—180°, which also resembles (II), are similarly obtained from Me isoneoxanthobilirubate (VI). $\text{Pb}(\text{OAc})_4$ oxidation of (V) and (VI) also gives 1' : 8'-dihydroxy-1 : 3 : 6 : 8-tetramethyl-2 : 7-diethyl-, m.p. 253° (corr.), and -2 : 3 : 6 : 7-tetramethyl-1 : 8-diethyl-, m.p. 242° (corr.), -4 : 5-di- β -carbomethoxyethylidipyrromethene, respectively (nomenclature: A., 1939, II, 229). The pyrromethene, m.p. 168° (darkens 145—150°), from 4-methyl-3-ethylpyrrole-2-aldehyde and opsopyrrolecarboxylic acid in AcOH-48% HBr, with Br-AcOH affords 5 : 5'-dibromo-3 : 4'-dimethyl-3'-ethyl-4- β -carbomethoxyethylpyrromethene hydrobromide, m.p. >310° (sinters 175°), which with MeOH-KOMe at 170—180° yields (III), glaucobilin, and mesobilipurpurin. Urobilin (and mesobilirubinogen), but no (I), is obtained by Na-Hg reduction of glaucobilin XIII α and mesobilirubin XIII α . Bilifuscin probably contains CH_2CH_2 in place of the Et of (I). H. B.

Myobilin. I. G. MELDOLESI, W. SIEDEL, and H. MÖLLER (Z. physiol. Chem., 1939, 259, 137—149).—The faeces (A) of myopathics contain myobilin (I) in addition to urobilin and stercobilin. (I) is a compound of mesobilifuscin (II) (preceding abstract) and protein; solutions exhibit a green fluorescence. The EtOH extract (room temp.) of (A) is mixed

with CHCl_3 , washed with H_2O , evaporated to a small vol., and then mixed with much light petroleum, thus pptg. (I). With MeOH-HCl, (I) gives the crude Me ester of (II); this is purified by hydrolysis (2% MeOH-NaOH), re-esterification, and chromatographic adsorption (Brockmann's Al_2O_3) whereby some (I) is recovered. H. B.

Constitution of cytochrome c. IV. Production of porphyrin-cysteine compounds. H. THEORELL (Biochem. Z., 1939, 301, 201—209; cf. A., 1939, II, 287).—Products obtained when 1 mol. of proto- or hæmato-porphyrin IX is heated at 100° for 72 hr. with 20% HCl and 6 mols. of *l*-cysteine (I) are very similar to or identical with the product obtained by heating porphyrin c for 5 hr. at 100° with 25% HCl. Very probably (I) reacts with the $\text{CH}_2\text{:CH}$ or $\text{OH}\cdot[\text{CH}_2]_2\cdot$ of the porphyrins and no interaction with (I) occurs when mesoporphyrin IX is used. The complex Fe compounds of the porphyrin-(I) compounds yield 30—50% of the theoretical amount of hæmatoporphyrin when treated with HBr-AcOH. c-Hæmins from cytochrome c behave in the same way. W. McC.

4-Lauryl- and 4- Δ^{10} -undecenoyl-morpholine.—See B., 1939, 647.

Nicotinmorpholamide.—See B., 1939, 665.

Reaction between organic compounds containing sulphur and hydrogen peroxide. XI. Cyclic sulphur compounds. R. KITAMURA (J. Pharm. Soc. Japan, 1938, 58, 8—114).—It is shown that if S is present as a member of an alicyclic ring and the vicinal C or N has a double linking the ring suffers fission under the action of H_2O_2 and O instead of S is added to one of these atoms. If, therefore, only a single vicinal atom has a double linking, ring fission takes place with production of a sulphonic acid whereby this atom adds O. The examples cited are : propylene- ψ -thiocarbamide to $\text{SO}_3\text{K}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$; ψ -thiohydantoin to $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$; 2 : 4-diketothiazolidine to $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$; rhodanine to 2 : 4-diketotetrahydrothiazole and thence to $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$; *N*-phenyl- ψ -thiohydantoin to $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$. If each of the atoms vicinal to S has a double linking, the compound is desulphurised; S is oxidised quantitatively to H_2SO_4 and addition of O occurs at both atoms. The substances examined from this viewpoint are oximino- ψ -thiohydantoin, oximino-*N*-phenyl- ψ -thiohydantoin [4-keto-5-oximino-2-anilotetrahydrothiazole], decomp. ~210°, thiophthalic anhydride, 2-anilo-3-methyl-, 2-allylimino-3-methyl-, and 3 : 5-dimethyl-1-allyl-1 : 3 : 4-thiodiazoline. If S is a member of an aromatic ring no such action occurs since the unusual double linking of an aromatic ring cannot add H_2O_2 . Thiophen, 2-anilino-, 2-allylamino-, and 2-allylamino-5-methyl-1 : 3 : 4-thiodiazole, and 3 : 5-diphenyl-1 : 2 : 4-thiodiazole are unaffected by alkaline H_2O_2 whilst 2-thiol- is transformed into 2-hydroxy-benzthiazole. H. W.

Reaction between thiosemicarbazones and maleic anhydride. J. M'LEAN and F. J. WILSON (J.C.S., 1939, 1048—1050; cf. A., 1937, II, 264).—

With maleic anhydride in C_6H_6 or PhMe, the thiosemicarbazones of $COMe_2$, $COPhMe$, 3-methylcyclohexanone, and PhCHO yield 2:4-diketotetrahydrothiazole-2-isopropylidene-, m.p. 233°, - α -phenylethylidene- (I), m.p. 244°, -3'-methylcyclohexylidene-, m.p. 209°, and -benzylidene-hydrazone-5-acetic acid, m.p. 255°; the δ -phenylthiosemicarbazones of the above ketones and of cyclohexanone yield 2:4-diketo-3-phenyltetrahydrothiazole-2-isopropylidene-, m.p. 175—180°, - α -phenylethylidene-, m.p. 185°, -3'-methylcyclohexylidene-, m.p. 192°, -benzylidene-, m.p. 215°, and -cyclohexylidene-hydrazone-5-acetic acid, m.p. 218° (decomp.), whilst the δ -methylthiosemicarbazones of $COPhMe$ and PhCHO yield 2:4-diketo-3-methyltetrahydrothiazole-2- α -phenylethylidene- (II), m.p. 154°, and -benzylidene-hydrazone-5-acetic acid, m.p. 188°. cycloHexanone- and 3-methylcyclohexanone- δ -phenyl-, and acetophenone- δ -methyl-thiosemicarbazone have m.p. 114°, 139°, and 135°, respectively. When hydrolysed by conc. HCl, (I) yields 2:4-diketotetrahydrothiazole-5-acetic acid, $N_2H_4 \cdot 2HCl$, NH_4Cl , and resin, whilst (II) gives analogous products. A. Li.

Preparation of 2-hydroxy-6-methylthionaphthen and its condensation with isatin. S. K. GUHA (J. Indian Chem. Soc., 1939, 16, 219—222).—Molten *o*-tolylthioglycolic acid with P_2O_5 at 150—160°/1 hr. affords 2-hydroxy-6-methylthionaphthen, m.p. 68—69°, which with isatin in boiling $AcOH-HCl$ gives 3-indole-2'-(7'-methyl)thionaphthen-indigo [3-keto-2-oxindolidene-7-methyl-2:3-dihydrothionaphthen], m.p. 314°, which dyes wool red from an acid bath and cotton light red from a hyposulphite vat. The shade of the dye is lighter than that of the parent substance (cf. A., 1939, II, 90). J. L. D.

Cyanine dyes.—See B., 1939, 667, 780.

Preparation of 4'-cyanines. (Miss) F. M. HAMER (J.C.S., 1939, 1008—1013).—In the 2:4'-cyanine condensation, by changing the mol. proportions of quinaldine methiodide, quinoline ethiodide, and alkali hydroxide from 1:2:1.2 to 1:3:3, the yield has been raised from 37 to 76—82%. K_2CO_3 is applicable to this condensation, but when the same dye is prepared from lepidine ethiodide and 2-iodoquinoline ethiodide, alkali hydroxide produces a 60% yield, whereas K_2CO_3 or NMe_3 produces 76%. Although 1-methylbenzthiazole alkiodide, when condensed with quinoline alkiodide, gave only 7—13% of thia-4'-cyanine, it is now condensed with 4-cyanoquinoline alkiodide [ethiodide, m.p. 200° (decomp.)] to give 30—37%: 1'-methyl-2-ethylthia-4'-cyanine iodide [(1-methyl-4-quinoline)(2-ethyl-1-benzthiazole)-methylcyanine iodide], m.p. 275° (decomp.), and 2:1'-diethylthia-4'-cyanine iodide. From the appropriate reagents the following are similarly prepared: 5-chloro-1'-methyl-2-ethylthia-, m.p. 292° (decomp.) and 1'-methyl-2-ethylsena-4'-cyanine iodide, m.p. ~285° (decomp.); 2:1'-dimethylthia-2'-cyanine iodide; 5:4'-(1'-methyl-1':4'-dihydroquinolylidene)-3-ethylrhodanine, m.p. 269°; and 1:4'-(1'-methyl-1':4'-dihydroquinolylidene)-2-keto-1:2-dihydrothionaphthen, m.p. 207—208°. When 4-chloroquinoline is heated with EtI, it does not simply give its ethiodide, m.p. 191° (decomp.) (Kaufmann *et al.*, A., 1912, 1, 502), but also 4-iodoquinoline ethiodide, decomp.

~234°, if the heating is carried out in a sealed tube. 4-Iodo- and 4-chloroquinoline methiodide, decomp. 208°, are similarly obtained. F. R. S.

Lupin alkaloids. XVII. Attempted synthesis of allolupinine. K. WINTERFELD and F. W. HOLSCHNEIDER (Arch. Pharm., 1939, 277, 192—203; cf. A., 1939, II, 129).—The attempted synthesis failed. The structure of *l*-lupinine (I) is confirmed by its oxidation (CrO_3) to isomeric lupinic acids (hydrochlorides, m.p. 255°, $[\alpha]_D +64.25^\circ$, and m.p. 130°, $[\alpha]_D -10.25^\circ$) (Steinsiek, Diss., 1928; cf. Schöpf, A., 1928, 1144). The prep. of 4 C_5H_5N -acids (Winterfeld *et al.*, A., 1931, 370) shows presence of allolupinine in impure (I). 2- $\gamma\gamma\gamma$ -Trichloro- β -hydroxy-*n*-propylpyridine (modified prep.) and alkali give 2-pyridylacrylic acid (with H_2-Pd -black gives oils), the hydrochloride of which is reduced by $H_2-Pd-BaSO_4$ in H_2O to β -2-pyridylpropionic acid (acid chloride could not be obtained). 2-Piperidylpropionyl chloride hydrochloride, m.p. 118—120°, is obtained from the acid hydrochloride by $SOCl_2$; with $CHNa(CO_2Et)_2$ it gives oils. R. S. C.

1:3-Dimethylxanthine-papaverine. A. MOSSINI (Boll. Chim. farm., 1939, 78, 261—262).—The f.p. of mixtures of theophylline and papaverine indicates the formation of a 1:1 complex, m.p. 212° (uncorr.). F. O. H.

Alkaloids of fumariaceous plants. XXI. *Corydalis lutea* (L.), DC. XXII. *Corydalis ochroleuca*, Koch. R. H. F. MANSKE (Canad. J. Res., 1939, 17, B, 89—94, 95—98).—XXI. The isolation of seven alkaloids from *C. lutea* (L.), DC, is described; of these protopine (I), *l*-tetrahydropalmatine (II), *l*-isocorypalmine (III), and isocorydine (IV) have been obtained from other sources. The occurrence of (IV) unaccompanied by corydine appears unique. A further alkaloid has been identified as *l*-stylopine (V), m.p. 206°, $[\alpha]_D^{25} -178^\circ$ in $CHCl_3$. Oxidation of (V) with I to the quaternary (coptisine) iodide followed by reduction yields *dl*-tetrahydrocoptisine. The suggestion that (II) is identical with *l*-tetrahydrocoptisine is confirmed; it is proposed to retain the name "stylopine." *Ochrobirine* (VI) (alkaloid F14), m.p. 198°, $[\alpha]_D^{25} +35.9^\circ$ in $CHCl_3$, or (+1MeOH) m.p. 138—139° (decomp.) (acetate, m.p. 177°), contains an esterifiable, non-phenolic OH and may possibly be 13-hydroxyprotopine. *Luteanine* (alkaloid F44), $C_{20}H_{23}O_4N$, m.p. 183°, is isomeric with cularine, which it resembles in containing 3 OMe and an indifferent O. It is suggested that the nature of the chemical constituents (in this case alkaloids) offers a possible means of determining interrelationships within a family. The close relation between *C. lutea*, *C. claviculata*, and *C. ochroleuca*, which has been proposed on morphological grounds, is not evidenced in the alkaloidal constituents.

XXII. Eight alkaloids have been isolated from *C. ochroleuca*, Koch, of which (I), (II), (III), (VI), bicuculline, and *l*-corypalmine have been described from other sources. Alkaloid F45, $C_{20}H_{19}O_3N$, has m.p. 268° (decomp.); it does not contain OMe but is phenolic. Alkaloid F46, m.p. 227°, contains $HOCH_2$ and is probably not phenolic. H. W.

Silicotungstates of tropine and of its derivatives. R. HAZARD (Bull. Soc. chim., 1939, [v], 6, 1077—1088; cf. A., 1938, II, 73).—Silicotungstates from tropine (I), tropigenine, and tropine *N*-oxide are cryst., whilst those from the semicarbazone of tropinone, benzoyl-tropine (II) or ψ -tropine, chloro- or bromo-tropan are amorphous; ψ -tropine (III), tropinone, and ecgonine (IV) give amorphous ppts., transformed into crystals. The relatively slower transformation in the case of the ppt. from (IV), through hexagons to needles (stable), is illustrated photomicrographically. Solubilities in H₂O for the silicotungstates are given. That from (II) is very insol.; the cryst. forms are more sol. than the amorphous. Addition of picric acid (best), 4:1:2-OH·C₆H₄(NO₂)₂, or *m*-NO₂·C₆H₄·CHO, in H₂O or Et₂O, aids pptn. of crystals, *e.g.*, from (I) and (II).

A. T. P.

Ergot alkaloids. XVII. Dimethylindole from dihydrolysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1939, 128, 715—719).—Interaction of EtCHO with *m*-tolylhydrazine, followed by treatment of the hydrazone with ZnCl₂ at 160°, yields 3:4- (I), m.p. 117—118° (picrate, m.p. 182—183°), and 3:6-dimethylindole, m.p. 90—93° (picrate, m.p. 163—164°). Fusion of dihydrolysergic acid with KOH yields (I).

J. D. R.

Alkaloids of *Mitragyna speciosa*. I. Mitragynine. H. R. ING and C. G. RAISON (J.C.S., 1939, 986—990).—From the leaves of *M. speciosa* there has been isolated an alkaloid (picrate, m.p. 123—127°; methiodide) and mitragynine (I), C₂₂H₃₀O₄N₂ (possibly C₂₂H₃₂O₄N₂), m.p. 105—115° [picrate, m.p. 217—223° (decomp.); acetate, m.p. 175—176° (decomp.) (lit. 142°); cinnamate, m.p. 155° (decomp.); *H* fumarate, decomp. 190—200°; *s*-C₆H₅(NO₂)₂ compound, m.p. 146° (decomp.); monomethiodide, m.p. 211·5°]. (I) is the Me ester of a monocarboxylic acid, which contains two OMe but no NMe; it behaves as a mono-acid base. Hydrolysis of (I) with MeOH-KOH gives a monocarboxylic acid (II), C₂₁H₂₈O₄N₂ (Et₂O-insol.; picrate, m.p. 157°), containing two OMe, and a (OMe)₄-compound, C₂₃H₃₄O₅N₂ (Et₂O-sol.; picrate, m.p. 135—136°), which corresponds with the addition of MeOH to (I), and further heating with KOH-MeOH converts it into (II). KOH-EtOH with (I) yields (II) and a compound [picrate, m.p. 124—125°; methiodide (+EtOH), m.p. 145—146°]. Zn-distillation of (I) affords a mixture, from which a base, C₁₄H₁₄ON₂, m.p. 115—120° [picrate, m.p. 263—264° (decomp.); *p*-nitrobenzylidene derivative, m.p. 255°], is separated; this base is not identical with either *pyr*- or *ind-N*-methylharmine. F. R. S.

Alkaloids of *Artabotrys suaveolens*. G. BARGER and L. J. SARGENT (J.C.S., 1939, 991—997).—Artabotrine (I), C₂₀H₂₂O₄N, m.p. 185—186° [*Ac* derivative (+2H₂O), m.p. 97—99°, anhyd., m.p. 118—119°], suaveoline (II), C₁₆H₁₆(OH)₂(OMe)₂NMe, m.p. 232°, [α]_D²⁵ +164° in CHCl₃, and artabotrine (III), C₁₆H₁₁(OMe)(CH₂O₂)NH, [α]_D¹⁸ -18·9° in CHCl₃ (hydrochloride, m.p. 273—274°, [α]_D¹⁸ -41·8° ± 4·2° in EtOH; *NO*-derivative, m.p. 203—204°; *N*-Me derivative, m.p. 132—133°, [α]_D¹⁸ -53·8° in EtOH), have been isolated. Nascent CH₂N₂ with (I) gives

O-methylartabotrine methiodide, m.p. 254—255°, also obtained from KI and the methosulphate, m.p. 255—256° [from (I) and Me₂SO₄]. ClCO₂Et and (I) yield a product, m.p. 109—110°, which is optically inactive, showing that (I) belongs to the aporphine type. Artabotrine methiodide, m.p. 224—225°, with KOH affords artabotrine methine, m.p. 122—123°, [α]_D¹⁸ -183° in EtOH, catalytically reduced to the H₂-derivative, m.p. 80—81°; the methine is degraded (Hofmann) to NMe₃ and a trimethoxyvinylphenanthrol, m.p. 108—109°. Oxidation (KMnO₄) of (I) gives an acid, C₈H₃O₂(OMe)₂·CO₂H, m.p. 203—204°, not identical with 2:4-, 2:5-, or 3:4-dimethoxyphthalide- α -carboxylic acid. (I) is probably 10-hydroxy-4:5:6-trimethoxyaporphine. Nascent CH₂N₂ and (II) yield a methiodide, m.p. 245—246°; (II) is probably 4:10-dihydroxy-5:6-dimethoxyaporphine. The aliphatic 10-OH is not contained in (III), which is probably 2-methoxy-5:6-methylenedioxyaporphine and identical with the Me ether of anolobine. F. R. S.

Configuration of heterocyclic compounds. X. Optical resolution of 10-phenylphenoxarsine-10-oxide-2-carboxylic acid. M. S. LESSLIE (J.C.S., 1939, 1050—1054; cf. A., 1936, 1004).—Crystallisation of the morphine salt of 10-phenylphenoxarsine-10-oxide-2-carboxylic acid gave two fractions, m.p. 245—246° and 241—243°, [α]_D²⁰₆₁ -101·6° and -38·5° in MeOH, leading respectively to the *l*-acid, m.p. 313—315°, [α]_D²⁰₆₁ -36·2° in dil. aq. NH₃, and the *d*-acid, m.p. 312—314°, [α]_D²⁰₆₁ +43·5° in dil. aq. NH₃. The acids and salts racemise slowly at room temp. Reduction (SO₂ in dil. HCl or Na₂S₂O₄) of the active acids gave inactive phenylphenoxarsinecarboxylic acid. A. Li.

Mercuriation of substituted derivatives of thymol. I. Nitroso-derivatives. II. Chloro-derivatives. A. W. RUDDY and J. B. BURT (J. Amer. Pharm. Assoc., 1939, 28, 286—290, 290—294).—I. 6-Nitrosothymol with Hg(OAc)₂ in EtOH yields 2-acetoxymcuri-6-nitrosothymol (I), m.p. 147·5° (decomp.), converted into 2-chloromcuri- and 2-bromomcuri-6-nitrosothymol, m.p. 152—153° (decomp.), by aq. NaCl and HBr, respectively. In aq. NaOH, (I) with CO₂ gives thymol-2-(hydroxymcuri)-6-nitroso-oxide, m.p. 210° (decomp.), which, with aq. NaOH, affords 2-hydroxymcuri-6-oximinothymoquinone. Attempts to mercurate 5-nitrosocarvacrol failed.

II. 6-Chlorothymol with Hg(OAc)₂ in EtOH-AcOH affords 2-acetoxymcuri-6-chlorothymol, m.p. 175—176° (decomp.), converted by I into 2-iodothymoquinone, m.p. 59°, by aq. NaCl and NaBr into 2-chloromcuri-, m.p. 165° (decomp.), and 2-bromomcuri-6-chlorothymol, m.p. 156° (decomp.), respectively, and by aq. NaOH-CO₂ into thymol-2-(hydroxymcuri)-6-chloro-oxide, m.p. 185·5° (decomp.), which is more stable to alkali than is the corresponding NO-compound. F. O. H.

Mercuriated and brominated compounds of acet-*p*-phenetide. M. RAGNO (Annali Chim. Appl., 1939, 29, 148—151).—*p*-OEt·C₆H₄·NHAc and Hg(OAc)₂ at 140° give trimercuriacet-*p*-phenetide triacetate, decomp. 155°, and tetramercuriacet-*p*-phenetide tetra-acetate, decomp. 170° (liquid at 200°). These with Br-KBr give respectively tribromo-, m.p.

165°, and *tetrabromo-acet-p-phenetidine*, m.p. 268° (decomp.). E. W. W.

Organomercury compounds of vanillin. G. Rossi and M. Ragno (Annali Chem. Appl., 1939, 29, 146—147).—Vanillin and $\text{Hg}(\text{OAc})_2$ in aq. EtOH form *mercurivanillin acetate*, $\text{CHO} \cdot \text{C}_6\text{H}_4(\text{OH})(\text{OMe}) \cdot \text{HgOAc}$, converted by conc. H_2SO_4 into the corresponding *sulphate*. E. W. W.

Mercuration of thionaphthen. F. CHALLENGER and S. A. MILLER (J.C.S., 1939, 1005—1008).—Thionaphthen (I) with HgCl_2 gives a *dimercurichloride*, m.p. 279—281°, and with $\text{Hg}(\text{OAc})_2$ yields a *dimercuriacetate*, and a *mono-compound* (II), m.p. 207—208°, which with EtCOCl affords *2-thionaphthenyl Et ketone*, m.p. 82—83° (*semicarbazone*, m.p. 204—205°), also obtained from (I) and EtCOCl . The ketone is oxidised [$\text{K}_3\text{Fe}(\text{CN})_6 \cdot \text{KOH}$] to *thionaphthen-2-carboxylic acid*, m.p. 204—205°. Mercuration thus falls into line with bromination and nitration. With NaI or CaCl_2 , (II) gives *di-2-thionaphthenylmercury*, m.p. 322°. F. R. S.

Reactions between organo-lead compounds and some metallic halides. H. GILMAN and L. D. APPERSON (J. Org. Chem., 1939, 4, 162—168).— PbPh_4 (I) and AlCl_3 in light petroleum or hexane at 100° apparently react thus: (I) + $\text{AlCl}_3 \rightarrow \text{PbPh}_3\text{Cl}$ (II) + AlPhCl_2 (III); (I) + (III) \rightarrow (II) + AlPh_2Cl ; (II) + $\text{AlCl}_3 \rightarrow \text{PbPh}_2\text{Cl}_2$ (IV) + (III). (II) and AlCl_3 give (IV), which is unaffected by AlCl_3 . (II) heated in BuOH for 6 hr. gives (IV) + (I). PbEt_4 (V) reacts similarly to (I), but PbEt_2Cl_2 is not isolated, as it yields PbEt_3Cl (VI) + PbCl_2 + EtCl . AlEt_3 , AlEt_2Cl , and AlEtCl_2 are formed. In C_6H_6 the reaction affords some C_6Et_6 . Cleavage of (V) or (VI) is effected by AlEt_2Cl + AlEtCl_2 in light petroleum, or at 150°, respectively. $\text{AlCl}_3 \cdot \text{Et}_2\text{O}$ has m.p. 34°, b.p. 108°/2—3 mm.

[With M. LICHTENWALTER.] (V) and FeCl_3 in Et_2O give FeCl_2 (90% yield); (V) and FeCl_2 , FeI_2 , CoBr_2 , or NiBr_2 do not react. (V) and H_2PtCl_6 give Pt.

[With H. L. YABLONKY.] (V) and BiCl_3 in Et_2O give (?) BiEt_3 + BiEt_2Cl . PbPh_3 + AlCl_3 in light petroleum (in N_2) at 100° give (IV) + (II); excess of PbPh_3 gives (I). (II) and AlPh_3 at 100° (6 hr.) afford (I). $\text{Pb}(\text{C}_6\text{H}_4\text{Me-o})_3$ and AlCl_3 at 100° give PbCl_2 , $\text{PbCl}(\text{C}_6\text{H}_4\text{Me-o})_2$, and $\text{Pb}(\text{C}_6\text{H}_4\text{Me-o})_4$. A. T. P.

Splitting proteins by ultra-violet light.—See A., 1939, I, 426.

Kinetics of destruction of tyrosine combined in the egg-albumin molecule by ultra-violet radiant energy.—See A., 1939, I, 425.

Nickel "insulinate." R. NETTER (Bull. Soc. chim., 1939, [v], 6, 1042—1046).—Cryst. insulin (+ Zn), pptd. by picric acid (probably forms "insulin picrate"), is freed from the latter by repptn. from its solution in x-NH_3 by COMe_2 . The resulting amorphous insulin and $(\text{NH}_4)_3\text{PO}_4 \cdot \text{NiSO}_4 \cdot \text{COMe}_2$ (p_H regulated) afford Ni "insulinate" (rhombohedra) (cf. Scott *et al.*, A., 1935, 788), of similar properties and physiological action to Zn "insulinate". Ni is removed by pptn. from aq. HCl solution by picric acid (removed as above). A. T. P.

Cyclol theory and the structure of insulin. D. M. WRINCH (Nature, 1939, 143, 763—764).—A reply to criticisms, based on "vector maps," of the view that the insulin mol. has a C_2 cage structure. Vector maps are untrustworthy since the no. of observations used in their prep. is limited and incomplete. L. S. T.

"Intraglobular" reaction in protein solutions. D. L. TALMUD (Nature, 1939, 143, 762—763).—The results of Gralén and Svedberg (A., 1939, I, 320) on the sedimentation const. of the product of the reaction of ovalbumin with $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ are re-interpreted. They support, rather than disprove, the hypothesis of intraglobular protein reaction. L. S. T.

Action of peroxides on hæmoglobin.—See A., 1939, III, 741.

Dumas method for [determining] organic nitrogen. F. SHEA and C. E. WATTS (Ind. Eng. Chem. [Anal.], 1939, 11, 333—334).—The standard procedure is modified to give good results with relatively unstable liquid compounds by replacing the usual pure CuO by a 1 : 1 mixture of CuO and CaCO_3 and the Cu gauze by short lengths of Cu wire. A modified nitrometer is used and CO_2 obtained from solid CO_2 . F. N. W.

Pregl sulphur combustion of metallic compounds. J. F. ALICINO (Ind. Eng. Chem. [Anal.], 1939, 11, 298).—With org. S compounds of the metals accurate results can be obtained when SO_4^{--} is also determined in the residues left in the Pt boat. L. S. T.

Modified Pregl spiral tube for sulphur and halogen determinations. C. W. BEAZLEY (Ind. Eng. Chem. [Anal.], 1939, 11, 229—230).—A Pregl tube is cut so that one section with the Pt catalysts remains in the furnace, whilst the other can be removed to wash out the products of combustion, the two sections being united as a ground-glass joint. Analyses for S were made according to Saschek's method (A., 1937, II, 529). The same technique was applied to the gravimetric determination of the halogens. L. S. T.

Determination of sulphur and halogens in organic compounds by the combustion [method] of Grote and Krekeler. L. RAMBERG and B. BÄCKLUND (Svensk Kem. Tidskr., 1939, 51, 101—113).—The method of Grote and Krekeler (B., 1933, 290) for determining S and halogens in org. compounds has been thoroughly investigated and has been adapted to the micro-scale. The method is far superior to the normal Carius method. M. H. M. A.

Determination of formaldehydesulphoxylic acid by means of copper sulphate. L. SPITZER (Annali Chim. Appl., 1939, 29, 184—186).— $\text{OH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$ is determined by adding it to aq. $\text{CuSO}_4 \cdot \text{H}_2\text{SO}_4$, and determining residual Cu" by the KI and $\text{Na}_2\text{S}_2\text{O}_3$ method. E. W. W.

Determination of glycerol. N. SCHOORL (Pharm. Weekblad, 1939, 76, 777—782).—The Bertram-Rutgers method (cf. A., 1938, II, 343) is improved. 10 c.c. of glycerol solution containing ≥ 0.5 g. are mixed with 10 c.c. of 7.5N-NaOH and 60 c.c. of

methylated spirit and the mixture is treated, with shaking, with small amounts of 10% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (I) in EtOH until a definite ppt. of $\text{Cu}(\text{OH})_2$ persists. An equal vol. of (I) is added with shaking, and the mixture made up to 100 c.c. with spirit. Next day the clear liquid is siphoned off. 50 c.c. are evaporated until free from EtOH, 10 c.c. of 4N- H_2SO_4 and 10 c.c. of 10% KI solution are added, and the liberated I is titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$. 1 c.c. = 9.2 mg. of glycerol). S. C.

Determination of amino-nitrogen by a copper method. C. G. POPE and M. F. STEVENS (Biochem. J., 1939, 33, 1070—1077).—The method depends on the formation of sol. Cu compounds from NH_2 -acids and excess of Cu present as $\text{Cu}_3(\text{PO}_4)_2$, the amount of Cu taken into solution being determined iodometrically. Quant. results are obtained with NH_2 -acids giving sol. Cu salts. Cystine, methionine, tryptophan, leucine, and phenylalanine, which form insol. Cu salts, can be determined if previously mixed with known amounts of glycine or aspartic acid in the ratio 1:4. Proline and hydroxyproline are also determined by the method, and NH_3 does not interfere. With histidine the results must be multiplied by 0.75 to give the α - NH_2 -N val.; with lysine, the ϵ -group is not determined. With enzymic digests and protein hydrolysates (20% HCl), the Cu compounds are completely sol. and the method gives good results.

J. N. A.

Volumetric determination of organic picrates and picrolonates with methylene-blue. A. BOLLIGER (Analyst, 1939, 64, 416—418).—The picrate is titrated with 0.001N-methylene-blue (I), the picrate of (I), which is sparingly sol. in H_2O , being extracted with CHCl_3 . Since (I) is not appreciably extracted by CHCl_3 , the end-point is given by the colour of the aq. layer. Sparingly sol. picrolonates are made sol. by boiling with (not an excess of) aq. Li_2CO_3 .

E. C. S.

Azides as reagents for the identification of phenols. XII. 3:5-Dinitro-4-methylbenzazide. P. P. T. SAH. XIII. *p*-Bromobenzazide. P. P. T. SAH and P. Y. CHENG. XIV. *p*-Nitrobenzazide. P. P. T. SAH and S. H. CHIAO (Rec. trav. chim., 1939, 58, 582—590, 591—594, 595—599).—*p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO}_2\text{H}$, conveniently prepared by oxidation (dil. HNO_3) of *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{COMe}$, with HNO_3 (*d* 1.52) gives 2:6:1:4-(NO_2) $_2\text{C}_6\text{H}_2\text{Me} \cdot \text{CO}_2\text{H}$ (amide, m.p. 188—190°), the *Me*, m.p. 85° (uncorr.), or *Et* ester, m.p. 68—70° (uncorr.), of which with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ -EtOH gives 3:5-dinitro-4-methylbenzhydrazide, m.p. 198—200° (uncorr.) [*CMe* $_2$ ·, m.p. 184—185° (uncorr.)], and *CHPh*·, m.p. 245° (uncorr.), derivatives], converted by aq. NaNO_2 -AcOH into the azide (I), decomp. 45—46°. *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$, through the hydrazide, affords *p*-nitrobenzazide (II). (I), *p*-bromobenzazide, or (II), with the following phenols in boiling ligroin, give excellent yields of 3:5-dinitro-4-methylphenyl-, *p*-bromophenyl-, or *p*-nitrophenyl-urethane, respectively (m.p. of urethanes are given in this order): PhOH , m.p. 174°, 152—153°, 167°; *o*-, m.p. 190—191°, 161—162°, 162°, *m*-, m.p. 187—188°, 124—126°, 143°, and *p*-cresol, m.p. 201°,

210—212°, 214°; 3:4:1-, m.p. 196—197°, 188—189°, 168°, 2:4:1-, 186—187°, 160—161°, 171°, and 2:5:1- $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{OH}$, 203—204°, 150—151°, 153°; *o*-, m.p. 180—181°, 141—143°, 143°, *m*-, m.p. 174—176°, 121—123°, 144°, and *p*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{OH}$, m.p. 212—213°, 196—197°, 196°; *o*-, m.p. 151—153°, 168°, 140°, *m*-, m.p. 164°, 123—125°, 137°, and *p*- $\text{C}_6\text{H}_4\text{Br} \cdot \text{OH}$, m.p. 212—213°, 204—205°, 198°; *o*-, m.p. 192°, 146°, 144°, *m*-, m.p. 167°, 144°, 167°, and *p*- $\text{C}_6\text{H}_4\text{I} \cdot \text{OH}$, m.p. 207°, 216—217°, 213°; *o*-, m.p. 127°, 145—146°, 190°, *m*-, m.p. 190°, 162—164°, 225°, and *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, m.p. 205—206°, 171—173°, 232°; 2:4:1- $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{OH}$, m.p. 157°, 169°, 205°; 2:4:1- $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{OH}$, m.p. 160—161°, 152°, 186°; *s*- $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{OH}$, m.p. 201—202°, 162—164°, 166°; *s*- $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{OH}$, m.p. 196—198°, 190—192°, 198°; *o*-, m.p. 138—139°, 145—146°, 157°, *m*-, 129—130°, 122—123°, 130°, and *p*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, m.p. 164°, 190—191°, 189°; α -, m.p. 225°, 148—149°, 189°, and β - $\text{C}_{10}\text{H}_7 \cdot \text{OH}$, 193—194°, 190—192°, 182°; thymol, m.p. 141—142°, 143—145°, 154°; *iso*-thymol, m.p. 168°, 136—137°, 143°; *Me*, chars with decomp. at 275—280°, 280—282°, >300° (chars), *Et*, chars and decomp. 260—264°, 270—272°, 270—271° (decomp.), and benzyl salicylate, m.p. 135—136°, 243° (decomp.), 179° (chars). The excellent yields and m.p. of the urethanes suggest that the above reagents can be used as micro-reagents. M.p. are corr. unless stated.

A. T. P.

Determination of piperazine. A. CASTIGLIONI (Z. anal. Chem., 1939, 117, 25—26).—The sample is treated in the min. of H_2O with dil. HCl until acid to Congo-red. Excess of 10% aq. silicotungstic acid is added. After 7—8 hr., the ppt., $\text{C}_8\text{H}_{28}\text{O}_{42}\text{N}_4\text{W}_{12}\text{Si}$, is collected, washed with 200 c.c. of H_2O acidified with HCl, and ignited. Piperazine = 0.06046 \times residue. The method is better than the piperazine picrate process.

J. W. S.

Reactions of the group $\text{S} \cdot \text{C} \cdot \text{NH} \cdot \text{C} \cdot$ with specific affinity for silver.—See A., 1939, I, 430.

Micro-determination of hypoxanthine and xanthine.—See A., 1939, III, 804.

Determination of organic bases and alkaloids by means of Reinecke's salt. P. DUQUENOIS and (MLLE.) FALLER (Bull. Soc. chim., 1939, [v], 6, 998—1008).—Examples of reineckates of org. bases or alkaloids which are pptd. immediately, or after a time, or not at all, are recorded. Experimental details are given; e.g., 4% solution of Reinecke's salt at 0° reacts in slightly acid or in neutral medium (pH 4—4.5 is generally suitable), and the ppt. is dried at 40°. Solubilities of reineckates in cold EtOH or Et $_2\text{O}$ are given. The method is applied successfully in numerous cases, e.g., pilocarpine, trigonelline, and brucine. Some reineckates are hydrated, e.g., from quinine, +2 H_2O . The formula is usually $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]_n$, alkaloid, where $n = 1$ or 2. Microcryst. examination of reineckates permits detection of cocaine and its hydrolysis products, strychnine and brucine, morphine and similar alkaloids, etc. in mixtures. A colorimetric method of detection is described also.

A. T. P.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1939.

Laboratory experiments in organic chemistry. N. D. CHERONIS (J. Chem. Educ., 1939, 16, 165—170; cf. A., 1938, II, 122). L. S. T.

Colour and constitution of organic compounds from the viewpoint of modern physical theory. T. FÖRSTER (Z. Elektrochem., 1939, 45, 548—573).—A review. J. W. S.

Thermal decomposition of petroleum hydrocarbons into free radicals. B. L. EVERING (J. Amer. Chem. Soc., 1939, 61, 1400—1405).—The thermal decomp. of petroleum hydrocarbons in an apparatus essentially that of Rice *et al.* (A., 1932, 1108) gives free radicals, which are allowed to react with Pb mirrors, freshly formed by condensation of Pb vapour. The concn. of free radicals formed was determined by determination of Pb in the Pb alkyl. In the pressure range 0.25—6.0 mm. the concn. of free radicals decreases with pressure but is not affected by the mol. wt. of the hydrocarbon which is decomposed, by dilution of the hydrocarbon stream with N₂, or by increasing the surface to vol. ratio.

Halogenation in reactive solvents. II. Addition of halogen and acetoxy to ethylene. F. C. WEBER, G. F. HENNION, and R. R. VOGT (J. Amer. Chem. Soc., 1939, 61, 1457—1458; cf. A., 1938, II, 388).—Chlorination of C₂H₄ in AcOH or MeOAc, using low concns. of Cl₂, gives C₂H₄Cl₂ and 29.6—44.7% of CH₂Cl·CH₂·OAc (I). In Ac₂O the yield of (I) is 16.9% at 10—15° and 87.1% at 40—43°. By-products are (CH₂·OAc)₂ (in AcOH), AcCl (in Ac₂O), or CCl₃·CH₂·OAc + MeCl (in MeOAc). R. S. C.

Reaction of propylene with isoolefines in the presence of sulphuric acid. V. N. IPATIEV, H. PINES, and B. S. FRIEDMAN (J. Amer. Chem. Soc., 1939, 61, 1825—1826).—C₃H₆ in 96% H₂SO₄ at 0° or 25°, with or without CuSO₄ or HgSO₄, gives Pr^δHSO₄ and only traces of hydrocarbons. However, passage of mixed C₃H₆ and CH₂:CMe₂ into H₂SO₄ gives 8—35% of hydrocarbons utilising C₃H₆, the exact amount depending on the concn. of the acid, temp., and mode of addition of the gas; the products are shown by hydrogenation, followed by fractionation and identification by b.p., *n*, *d*, and Raman spectra, to be CH₂:CH·CH₂Bu^γ and CH₂:CMeBu^γ (from 2Pr^δHSO₄), and a βγ-dimethylpentene (formed by isomerisation of the other products); the H₂SO₄ contains Pr^δHSO₄, but no Bu^γHSO₄. C₃H₆ and iso-pentenenes give, when mixed, similarly 16% of C₈H₁₆ and 17% of C₁₃H₂₆, but admixture with *n*-butenes is ineffective. Passage of the olefine mixture into Pr^δHSO₄ is more effective than into H₂SO₄.

R. S. C.

Stereoisomerism of unsaturated compounds. IV. Identification of *cis-trans* isomerides by rate studies. W. G. YOUNG, D. PRESSMAN, and C. D. CORYELL. V. Mechanism for the formation of butenes from βγ-dibromobutanes by the action of iodide ion. S. WINSTEIN, D. PRESSMAN, and W. G. YOUNG (J. Amer. Chem. Soc., 1939, 61, 1640—1644, 1645—1647; cf. A., 1937, II, 132).—IV. The kinetics of the reaction CHRBr·CHR'Br + 3I⁻ → CHR:CHR' + I₃⁻ + 2Br⁻ at ~59° and ~75° are reported and discussed in detail for the dibromides from *cis*- and *trans*-(·CHMe)₂, -CHMe:CHEt, -(·CHEt)₂, and -(·CHPr^a)₂, maleic and fumaric acids. In all cases in which R = or is similar to R', the *trans*-derivative reacts faster than the *cis* and has a smaller heat of activation.

V. Elimination of Br from (CHMeBr)₂ (I) by I in aq. PrOH at ~95° or O(CH₂·CH₂·OH)₂ at ~200° is largely *trans*. Thus, *meso*-(I) gives 96%-pure *trans*-C₄H₈, and *dl*-(I) gives 91%-pure *cis*-C₄H₈; the nature of the C₄H₈ is proved by conversion into the dibromide and measurement of its rate of reaction with I. Details of the reaction mechanism are discussed.

R. S. C.

Addition of hydrogen halides to *cis*- and *trans*-Δ^δ-pentene. M. S. KHARASCH, C. WALLING, and F. R. MAYO (J. Amer. Chem. Soc., 1939, 61, 1559—1564).—*trans*- (prepared from CHMePr^aBr or CHET₂Br), *n*_D²⁰ 1.3797, and *cis*-Δ^δ-pentene (prepared from CMe:CEt by H₂-Pd-BaSO₄ in MeOH at 0°), *n*_D²⁰ 1.3823, add HBr alone, in AcOH, or in presence of NHPH₂, PhSH, C₆H₅Me·SH, FeBr₃, ascaridole, or Bz₂O₂ to give a 1:1 mixture of CHMePr^aBr and CHET₂Br. A similar mixture of chlorides is obtained by HCl in AcOH or in presence of FeCl₃. This mode of addition is due to the nearly equal activation energies of the two reactions, caused by the similarity of the Me and Et substituents on the C:C. The halide mixtures are analysed by *n* and formation of the anilides (mixed m.p. curves given). CH:CEt, b.p. 10—20°, is obtained in 64% yield from C₂H₂, Na, and Et₂SO₄ in liquid NH₃, and is converted into CMe:CEt by treatment in Et₂O first with MgEtBr and then with Me₂SO₄.

R. S. C.

Conjugated hexadienes. C. PRÉVOST (Compt. rend., 1939, 208, 1589—1591).—Propylvinyl- (I) and ethylpropenyl-carbinol when heated with Al₂O₃ at 360° or NaHSO₄ at 170° give mixtures of hexa-Δ^{δδ}-diene (II), hexa-Δ^{αγ}-diene (III), and hexa-Δ^{δδ}-diene (IV). In each case a trace to 2% of (II) is formed. When (I) is heated with NaHSO₄, mainly (III) (85%) is formed, although the total yield is low (45%). In the other reactions 83—94% of (IV) is formed. When (IV) is heated with Al₂O₃ at 360°,

some (III) is formed; at 450–480°, (III) (15%), (II) (20%), and penta- Δ^{γ} -diene (8%) are formed.

J. L. D.

Substituted acetylenes and their derivatives.

XXXII. Halogenation in reactive solvents. III. Chlorination of vinylacetylene in methanol.

A. A. BAUM, R. R. VOGT, and G. F. HENNION.

XXXIII and IV. Chlorination of Δ^{α} -hexinene in reactive solvents.

R. O. NORRIS, R. R. VOGT, and G. F. HENNION (J. Amer. Chem. Soc., 1939, **61**, 1458–1460, 1460–1461; cf. A., 1939, II, 197).—XXXII. Passage of $\text{CH}_2\text{:CH:C:CH}$ (I) into MeOH at 30° and of Cl_2 over the surface so that only a slight excess of Cl_2 is present causes the following reactions: (I) \rightarrow α -chloro- β -methoxy- Δ^{γ} -butadiene (II) (10%), b.p. 57.4–57.6°/48 mm. \rightarrow

$\text{CH}_2\text{:CH:C(OMe)}_2\text{CHCl}_2 \rightarrow (+\text{HCl})$ $\alpha\delta$ -trichloro- $\beta\beta$ -dimethoxybutane (III) (20%), b.p. 103°/3 mm.;

(II) $\rightarrow \text{CH}_2\text{:CH:CCl(OMe)CHCl}_2 \rightarrow \text{MeCl} +$

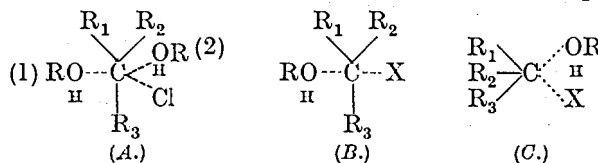
$\text{CH}_2\text{:CH:C(OMe)CHCl}_2 \rightarrow \alpha\delta$ -trichlorobutan-2-one (IV) (8%), b.p. 81.5–82.5°/18 mm. Only (II), (III),

(IV), and MeCl were isolated. (IV) does not give CO₂ reactions and gives the haloform reaction slowly. (III) is not readily hydrolysed, but hot AcOH containing a little H₂O and H₂SO₄ produces MeOAc. *n* and *d* of the products are given.

XXXIII. Passage of Cl_2 over $\text{CH}_2\text{CBu}^{\alpha}$ in H₂O at 45±5° gives trans- $\alpha\beta$ -dichloro- Δ^{α} -n-hexene (V) (20%), b.p. 55–57°/25 mm., $\alpha\alpha\beta$ -trichloro-n-hexane (VI) (20%), b.p. 90–93°/10 mm., $\alpha\alpha\beta\beta$ -tetrachloro-n-hexane (VII) (28%), b.p. 108–110°/10 mm., and CHCl_2 Bu ^{α} ketone (VIII) (20%), b.p. 63–65°/11 mm. In AcOH cis- $\alpha\beta$ -dichloro- Δ^{α} -n-hexene (IX) (23%), b.p. 80–82°/25 mm., (VI) (18%), (VII) (7%), (VIII) (34%), and AcCl (20%) [produced with (VIII) by fission of $\text{OAc:CBu}^{\alpha}\text{Cl:CHCl}_2$] are formed. In Ac₂O (IX) (5%), (VI) (12%), (VII) (26%), (VIII) (43%), and AcCl (100%) (produced by fission of the primary additive product, $\text{Ac}_2\text{O} \rightarrow \text{CBu}^{\alpha}\text{:CH} \rightarrow \text{Cl}_2$) are formed. No oxygenated products are obtained in Bu ^{α} OH or MeOAc. In Bu ^{α} OH some Bu ^{α} OCl must be formed to act as source of HCl, the products being (V) (102%) and (VI) (23%). In MeOAc the products are (IX) (35%), (I) (7%), (VI) (19%), (VII) (28%), and $\alpha\alpha\beta\beta$ -pentachloro-n-hexane (48%), b.p. 129–131°/10 mm. The factors influencing production of (V) and/or (IX) are obscure. The structures of (V) and (IX) are determined by dipole moments, which are 0.57 and 1.993×10^{-18} e.s.u., respectively. *n* and *d* of the products are given. R. S. C.

Solvolysis of *tert*-butyl chloride. Solvolytic reactions and the Walden inversion. S. WINSTEIN (J. Amer. Chem. Soc., 1939, **61**, 1635–1640).—Ingold's *S_N1* mechanism for the reaction, $\text{RHal} + \text{R'OH} \rightarrow \text{ROR'} + \text{HHal}$, is held to be inherently improbable, because, *inter alia*, the halogen ion split off would not protect the R⁺ ion sufficiently to force reaction to occur at the back of the C. The solvent (H₂O) is considered to play an essential part in such reactions, the mechanism being: (a) $\text{H}_2\text{O} + \text{>C:X} \rightarrow \text{H}_2\text{O}^+-\text{C} \leftarrow \text{X}^-$; (b) $\text{>C:X} + \text{OH}_2 \rightarrow \text{C}^+-\text{OH}_2 + \text{X}^-$; (c) $\text{H}_2\text{O} + \text{>C}^+-\text{OH}_2 \rightarrow \text{H}_2\text{O}^+-\text{C} \leftarrow \text{OH}_2$; (d) $\text{>C}^+-\text{OH}_2 \rightarrow \text{>C}^+-\text{OH} + \text{H}^+$; (e) $\text{H}_2\text{O}^+-\text{C} \leftarrow \text{OH} \rightarrow \text{OH}^+-\text{C} \leftarrow + \text{H}^+$.

Reaction (a) involves reversal of configuration, whereas (b) involves its retention. (c) is racemisation. The rates and products of hydrolysis of Bu ^{γ} Cl in aq. CMe₂ and aq. dioxan and of its alcoholysis (MeOH, EtOH) are accounted for by equations, based on fugacities, involving either 2 or 3 solvent mols. (cf. Olson *et al.*, A., 1938, I, 86; Bateman *et al.*, A., 1938, II, 304). Reaction is thus essentially bimolecular. (cf. Hammett *et al.*, A., 1938, II, 86, 87), the usual transition state being (A); solvent mol. (1) finds its place by attack away from the Cl; solvent mol. (2) becomes attached because of the tendency to form H–Cl linkings. Removal of mol. (2) results in inversion, and removal of mol. (1) results in retention of configuration. Formation of (A) accounts for the reaction (c). With very low concn. of H₂O



in, e.g., CMe₂, reaction becomes bimol., the transition states for inversion and retention of configuration being (B) and (C), respectively. Other first-order reactions are briefly discussed from a similar viewpoint. Solvolysis of CHPh₂Cl and CHPhMeCl is similar to that of Bu ^{γ} Cl. R. S. C.

Peroxide effect in the addition of reagents to unsaturated compounds. XX. Addition of hydrogen bromide to Δ^2 -butinene and β -bromo- Δ^2 -butene. C. WALLING, M. S. KHARASCH, and F. R. MAYO (J. Amer. Chem. Soc., 1939, **61**, 1711–1713).—Abnormal addition to a non-terminal ethylenic linking is achieved by unsymmetrical distribution around it. (:CMe)₂ (prop. modified), b.p. 27.0–27.4°, m.p. –28° to –27°, adds HBr (no solvent) only normally to give CMeEtBr₂, whether peroxides or antioxidants are present. With ascaridole in C₃H₁₂ only abnormal addition occurs, giving (CHMeBr)₂. In AcOH presence of peroxides or antioxidants controls the results. The unsymmetrical loading occurs at the intermediate stage, CHMe:CMeBr. The effect of the presence and nature of the solvent is remarkable. R. S. C.

Treatment of neopentyl halides with mercury di-*p*-tolyl. F. C. WHITMORE and E. ROHRMANN (J. Amer. Chem. Soc., 1939, **61**, 1591–1592).— $\text{CH}_2\text{Bu}^{\gamma}\text{Br}$ and $\text{Hg}(\text{C}_6\text{H}_4\text{Me-p})_2$ at 200° (20 hr.) react only very slightly, giving ~5% of olefines, mainly CHMe.CMe₂. $\text{CH}_2\text{Bu}^{\gamma}\text{I}$ also reacts very slightly (7–9%), but gives only 0.7% of olefines. $\text{CH}_2\text{Bu}^{\gamma}\text{I}$ and HgCl_2 in Et₂O–N₂ give 23.5% of *Hg dineopentyl*, m.p. 31–33°, b.p. 67–69°/3 mm., and some $\text{HgCl} \cdot \text{CH}_2\text{Bu}^{\gamma}$. R. S. C.

Reaction of neopentyl chloride with sodium. F. C. WHITMORE, A. H. POPKIN, and J. R. PFISTER (J. Amer. Chem. Soc., 1939, **61**, 1616–1617).— $\text{CH}_2\text{Bu}^{\gamma}\text{Cl}$ and Na (1 atom) give 36% of CMe₄, 25% of 1:1-dimethylcyclopropane, b.p. 19.8°/740 mm., and 13% of (CH₂Bu ^{γ})₂. R. S. C.

Preparation of neopentyl iodide and bromide. F. C. WHITMORE, E. L. WITTE, and B. R. HARRIMAN (J. Amer. Chem. Soc., 1939, **61**, 1585–1586).—

$\text{CH}_2\text{Bu}^\gamma\text{OH}$, red P, and I give only 4–9% of iodide (cf. Ingold *et al.*, A., 1933, 262). $\text{CH}_2\text{Bu}^\gamma\text{Cl}$ (prep. in 30% yield from CMe_4 by Cl_2), b.p. $83.3^\circ/740$ mm., readily gives the Mg derivative, which with HgCl_2 in Et_2O yields 90% of $\text{MgCl}\cdot\text{CH}_2\text{Bu}^\gamma$, m.p. $117\text{--}118^\circ$. With aq. I–KI this gives 92% of $\text{CH}_2\text{Bu}^\gamma\text{I}$, b.p. $132.6^\circ/734$ mm., stable, and with Br gives 82% of $\text{CH}_2\text{Bu}^\gamma\text{Br}$, b.p. $105^\circ/732$ mm. No rearrangement occurs. $\text{MgCl}\cdot\text{CH}_2\text{Bu}^\gamma$ and I in Et_2O give $\text{CH}_2\text{Bu}^\gamma\text{I}$ contaminated with the alcohol and hydrocarbons. $\text{CH}_2\text{Bu}^\gamma\text{I}$ is much less reactive than Bu^γI . R. S. C.

Chemistry of vitamin-E. IX. Preparation of long-chain halides and ketones containing iso-pentane units. L. I. SMITH, H. E. UNGNADE, F. L. AUSTIN, W. W. PRICHARD, and J. W. OPIE (J. Org. Chem., 1939, 4, 334–341).—The complete hydrogenation of geraniol requires a temp. of 200° and initial pressure 2550 lb. Reaction occurs in two well-defined stages. Citronellol, from which the allylic double linking is absent, is much more readily reduced completely ($125^\circ/1900$ lb.) whilst farnesol requires $200^\circ/2700$ lb. for complete reduction. The only methods suitable for the conversion of these unsaturated and saturated alcohols into their halides involve the use of dry H halide. For allylic alcohols good yields are obtained when the alcohol is saturated with dry HBr or HCl, preferably in the presence of a drying agent and kept in the cold, whilst the higher saturated alcohols give the best yields of halides (bromides) by treatment with a current of dry HBr at 150° without a solvent. Aq. HBr adds to the double linking of allylic alcohols so that dihalides are the main product. For the alkylation of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ with allylic halides dilution with light petroleum appears advantageous but with saturated halides the customary procedure may be followed. Hydrolysis of the esters to ketones is best effected with H_2O alone at 200° under high pressure of H_2 . $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{Cl}$ does not react with $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, which with $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{I}$ or preferably $\text{OEt}\cdot[\text{CH}_2]_2\cdot\text{Br}$ gives a modest yield of *Et*₂ ethoxyethylacetonedicarboxylate (I), b.p. $108\text{--}114^\circ/17$ mm. *Et*₂ perhydrogeranylacetonedicarboxylate has b.p. $145\text{--}155^\circ/0.1$ mm. (I) and perhydrogeranyl bromide (II) give a non-uniform product. (II) is converted by successive treatments with Mg and $\text{OMe}\cdot\text{CH}_2\text{Cl}$ into α -methoxy-80-dimethylnonane, b.p. $94\text{--}94.5^\circ/14.5$ mm., obtained with greater difficulty but in somewhat better yield from tetrahydrogeranyl chloride; it is best cleaved by dry HBr to the C₁₁ bromide. H. W.

Reaction steps in the conversion of $\beta\gamma$ -di-acetoxybutane into $\beta\gamma$ -dibromobutane. S. WINSTEIN and H. J. LUCAS (J. Amer. Chem. Soc., 1939, 61, 1581–1584).—Conversion of $(\text{CHMe}\cdot\text{OAc})_2$ into $(\text{CHMeBr})_2$ by aq. HBr is shown to proceed by way of $\text{OAc}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$ (I), $\text{OAc}\cdot\text{CHMe}\cdot\text{CHMeBr}$ (II), and $\text{OH}\cdot\text{CHMe}\cdot\text{CHMeBr}$, by (a) isolating these intermediates from the reaction mixture and (b) synthesising them and showing them to react with aq. HBr in the desired direction and at the correct speeds. The step (I) \rightarrow (II) is the only one at which inversion occurs, which explains why only one C is inverted during the whole series of changes. dl-threo- (III), b.p. $70.1^\circ/13$ mm., and dl-erythro- γ -Bromo- β -

acetoxybutane (IV), b.p. $67.2^\circ/13$ mm., are obtained from the corresponding bromohydrins by Ac_2O . dl-erythro- γ -Acetoxybutan- β -ol (V), b.p. $79.2^\circ/10$ mm., is obtained from the meso-glycol by Ac_2O and a little H_2O or, with an inversion, from trans- $\beta\gamma$ -epoxybutane (VI) by AcOH . meso- $(\text{CHMeBr})_2$ is obtained from (IV) or (VI). dl- $(\text{CHMeBr})_2$ is obtained from (III) or (V) (both sources). Reaction mechanisms are discussed. Conversion of $(\text{CHMe}\cdot\text{OAc})_2$ into $(\text{CHMeBr})_2$ by HBr in AcOH involves much inversion, but the reaction mechanism is obscure. R. S. C.

Intramolecular reaction between neighbouring substituents of vinyl polymerides. P. J. FLORY (J. Amer. Chem. Soc., 1939, 61, 1518–1521).—Statistical analysis shows that when the X of polymerides, $[\text{CH}_2\cdot\text{CHX}\cdot\text{CH}_2\cdot\text{CHX}]_n$ (I), interact to form rings, 13.53% of the X become isolated; 86.47% is thus the theoretical limit of the reaction. If the polymeride is a random mixture of (I), $[\text{CH}_2\cdot\text{CHX}\cdot\text{CHX}\cdot\text{CH}_2]_n$, and $[\text{CHX}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHX}]_n$ units, and if reaction of $\alpha\delta$ -substituents is impossible, 18.40% of the substituents become isolated. R. S. C.

Retention of configuration in the reaction of γ -bromobutan- β -ols with hydrogen bromide. S. WINSTEIN and H. J. LUCAS (J. Amer. Chem. Soc., 1939, 61, 1576–1581).—trans-, b.p. $53.5^\circ/742$ mm., and cis- $\beta\gamma$ -Epoxybutane (I), b.p. $59.7^\circ/742$ mm., give erythro- (II), b.p. $53.1^\circ/13$ mm. (3 : 5-dinitrobenzoate, m.p. 85° ; α -naphthylurethane, m.p. 133°), and threo- γ -bromobutan- β -ol (III), b.p. $50.5^\circ/10$ mm. (3 : 5-dinitrobenzoate, m.p. 109° ; α -naphthylurethane, m.p. 103°), respectively. (III) is also obtained from cis- Δ^8 -butene by NHBrAc . Aq. K_2CO_3 reconverts (III) into (I). 48% aq. HBr at 0° converts (II) and (III) into pure meso- and dl- $(\text{CHMeBr})_2$, respectively. Reaction mechanisms to explain the retention of configuration are discussed. R. S. C.

Hydrogenation of a higher secondary alcohol by nickel catalysts containing manganese, zinc, or thorium. K. KINO (J. Soc. Chem. Ind. Japan, 1939, 42, 188B).—Hydrogenation (Ni) of the alcohol obtained by reducing stearone removes the OH slowly at 200° , rapidly at 250° . The reaction is accelerated by Th, but not by Zn or Mn. A. LI.

Catalytic dehydration of $\text{C}_6\text{--}\text{C}_8$ aliphatic alcohols. S. GOLDWASSER and H. S. TAYLOR (J. Amer. Chem. Soc., 1939, 61, 1751–1761).—When passed over Al_2O_3 (various samples give the same results) at 398° , *n*- $\text{C}_6\text{H}_{13}\cdot\text{OH}$ (I) gives mainly Δ^2 -*n*-hexene, $\text{CH}_2\cdot\text{CMePr}^a$, and $\text{CHMe}\cdot\text{CHPr}^b$; $\text{CHEt}\cdot\text{CH}_2\cdot\text{OH}$ (II) gives mainly Δ^2 - and Δ^7 -*n*-hexene, $\text{CHMe}\cdot\text{CMeEt}$, $\text{CH}_2\cdot\text{CEt}_2$, and $\text{CHEt}\cdot\text{CMe}_2$; $\text{CHPr}^a\cdot\text{OH}$ (III) gives mainly Δ^7 -*n*-hexene, $\text{CH}_2\cdot\text{CEtPr}^a$, and $\text{CHPr}^a\cdot\text{CMe}_2$; $\text{CHMeBu}^b\cdot\text{CH}_2\cdot\text{OH}$ (IV) gives mainly $\text{CHMe}\cdot\text{CH}\cdot\text{CHMeEt}$, $\text{CHPr}^b\cdot\text{CMe}_2$, and $\text{CHMe}\cdot\text{CMePr}^b$; $\text{CHPr}^b\cdot\text{OH}$ (V) gives mainly $\text{CHEt}\cdot\text{CHPr}^b$, $\text{CHPr}^b\cdot\text{CMe}_2$, and $\text{CHMe}\cdot\text{CMePr}^b$; $\text{CHETBu}^a\cdot\text{CH}_2\cdot\text{OH}$ (VI) gives mainly $\text{CHBu}^a\cdot\text{CMe}_2$, $\text{CHMe}\cdot\text{CMeBu}^a$, $\text{CHEt}\cdot\text{CMePr}^a$, and Δ^7 -*n*-octene. The numerous secondary decomp. products are identified, their origin as secondary products being proved by their formation in larger amounts with longer times of contact. Much tar is also formed, the amount

increasing with the amount of alcohol recovered, *i.e.*, with increasing rate of passage; it is formed in competition with the dehydration, showing that the alcohol is more strongly adsorbed than the olefines and flushes the latter off the surface. The ease of dehydration is (II) > (III) > (I) > (IV) > (V). This order is not connected with the no. of H attached to the C-OH and is unintelligible if dehydration is from a CH₂ next to the C-OH; moreover, it correlates exactly with the no. of other H available sterically. The primary products are precisely accounted for if elimination of H₂O gives a cyclopropane derivative as labile intermediate, all the expected products from fission of the ring being found; moreover, they accord with the view that the ease of removal of H is from CH > CH₂ > Me. ThO₂ gives similar results, but ring-fission tends to occur more at one place. Cr₂O₃ causes also dehydrogenation, leading to aromatic products. The apparatus is a modification of that previously described (A., 1939, II, 305). R. S. C.

Spectrographic and chemical examination of some unsaturated alcohols and their dehydration products. I. β -Methylpentane- $\beta\delta$ -diol. G. DUPONT and (MLLE.) M. DARMON. II. Mesityl oxide and alcohol derivatives. G. DUPONT and (MLLE.) M. L. MENUT (Bull. Soc. chim., 1939, [v], 6, 1208—1214, 1215—1220).—I. Spectrographic examination and selective hydrogenation (NaNH₂) are used to determine the constitution of the unsaturated products. OH·CMe₂·CH₂·Ac is hydrogenated (Cu chromite) at 110—120° to β -methylpentane- $\beta\delta$ -diol, b.p. 192° (Raman spectra), which when distilled with NH₂Ph·HBr gives β -methyl- Δ^a -penten- δ -ol (I), b.p. 128—130°, a mixture (II), b.p. 75.5—76.5°, of *cis*- and *trans*- β -methyl- $\Delta^{a\gamma}$ -pentadiene, and a little β -methyl- $\Delta^{\beta\delta}$ -pentadiene (cf. Diels *et al.*, A., 1929, 819; Bacon *et al.*, A., 1937, II, 395). (II) is hydrogenated (Raney Ni or Pt) to a mixture of *cis*- and *trans*- δ -methyl- Δ^{β} -pentene. (II) and CHMe·CH·CHO give 5-aldehydo-2:4-dimethyl- Δ^1 -cyclohexene, b.p. 90—91°/20 mm. (semicarbazone, m.p. 182°), which with COMe₂ gives an isomeride, b.p. 134—135°/15 mm., of ionone (Raman spectra examined). (I) is hydrogenated to β -methylpentan- δ -ol (III), b.p. 128—130°.

II. Mesityl oxide (III), CHAc·CMe₂, from the dehydration (I, HBr, or CuSO₄) of OH·CMe₂·CH₂·Ac, contains some isomeride, CH₂·Ac·CMe·CH₂, the amount varying with the method of prep. (III) and MgMeBr afford mainly OH·CMe₂·CH·CMe₂ and ~20% of OH·CMe·CH₂·CMe·CH₂ (Raman spectra examined), readily dehydrated by NH₂Ph·HBr to CMe₂·CH·CMe·CH₂, b.p. 93—95°, hydrogenated (NaNH₂) to CHPr ^{β} ·CMe₂, b.p. 83—84°. Ponderff reduction of (III) gives, through a boric ester, b.p. 130°/15 mm., a mixture of CMe₂·CH·CHMe·OH, with ~20% of CH₂·CMe·CH₂·CHMe·OH, hydrogenated to (III). β -Methyl- Δ^a -penten- δ -ol is dehydrated (NH₂Ph·HBr) to β -methyl- $\Delta^{a\gamma}$ -pentadiene.

A. T. P.

Reactions relating to carbohydrates and polysaccharides. LVI. Synthesis of higher polyoxyethylene glycols. R. FORDYCE, E. L. LOVELL, and H. HIBBERT. LVII. Synthesis of 90-mem-

bered and 186-membered oxyethylene glycols. R. FORDYCE and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 1905—1910, 1910—1911; cf. A., 1938, II, 39).—LVI. Addition of (CH₂·OH)₂ to Na (1 atom) in MeOH at 40°, removal of the MeOH, and heating with (CH₂Cl)₂ (1.1 mol.) at 95° gives 48% of *hexaoxyethylene glycol* (I), OH·[CH₂·CH₂·O]₆·H, m.p. 2.1°, b.p. 185—185.7°/0.015 mm. The cryst. salt, OH·[CH₂]₂·ONa, + (CH₂·OH)₂, and CPh₃Cl in dioxan at 70° give β -triphenylmethoxyethyl alcohol, m.p. 116—116.5°, constituting a proof of structure. SOCl₂ in C₅H₅N at 45° converts (I) into the *dichloride*, m.p. -12.4°, b.p. 168—169°/0.1 mm., which with the K₁ salt of (I) in light petroleum (b.p. 100—110°), first at 65°, then at 135°, and finally at 175°, gives *octadecaoxyethylene glycol* (II), OH·[CH₂·CH₂·O]₁₈·H, m.p. 23.8°. The *dichloride* (prep. therefrom by SOCl₂ at 65°), m.p. 22.9°, of (II) with the K₁ salt of (II) [as for (II), but at 135°] gives *dotetracontaoxyethylene glycol* (III), OH·[CH₂·CH₂·O]₄₂·H, m.p. 33.8°. The derived *dichloride* has m.p. 33.4°. The purity of (I), (II), and (III) is proved by the regularity of *n* and, particularly, by the long flat portion of the cooling curve and the abrupt termination thereof.

LVII. The Na salt of (III) and dichloride of (I) give *nonacontaoxyethylene glycol* (IV), OH·[CH₂·CH₂·O]₉₀·H, birefringent, m.p. 40.6°, the Na salt of which with the dichloride of (I) gives the *glycol* (V), OH·[CH₂·CH₂·O]₁₈₆·H, m.p. 44.1°. The purity of (IV) and (V) is shown by cooling curves.

R. S. C.

Reactions relating to carbohydrates and polysaccharides. LVIII. Relation between chain length and viscosity of polyoxyethylene glycols. R. FORDYCE and H. HIBBERT. LIX. Precipitability of pure hemocolloidal polyoxyethylene glycols. E. L. LOVELL and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 1912—1915, 1916—1920; cf. preceding abstract).—LXVIII. Staudinger's equation, $\eta_{sp}/c = K_m M$, is shown to hold for the pure glycols, OH·[CH₂·CH₂·O]_{*n*}·H (*n* = 6, 18, 42, 90, and 186), except for low *n*. For low *n*, particularly, it is better replaced by $\eta_{sp}/c = K_m M + \beta$, β being the η_{sp}/c intercept on the graph. The relations between K_m and the mol. wt. (*M*) for the pure glycols and for Staudinger's mixed polyoxyethylene oxides are similar, but not identical, the difference being due to the non-homogeneity of the latter.

LIX. The relation between the "precipitability" (Schulz, A., 1937, I, 510) of the above glycols and *n* is determined for MeOH-Et₂O and dioxan-Et₂O, and a new quant. equation is postulated. The log of the solubility (%) \propto % Et₂O in the MeOH-Et₂O. The glycol (*n* = 186) behaves abnormally and indicates that pptn. may not always provide a regularly graded series of products.

R. S. C.

d-Arabitol in *Fistulina hepatica*.—See A., 1939, III, 733.

Tritylation experiments in the sugar alcohol series. M. L. WOLFROM, W. J. BURKE, and S. W. WAISBROT (J. Amer. Chem. Soc., 1939, 61, 1827—1829).—*l*-Fucitol with CPh₃Cl in C₅H₅N at 60°, followed by Ac₂O at 45°, gives *l*-fucitol 1-CPh₃ ether

2:3:4:5-tetra-acetate, m.p. 152°, $[\alpha]_D^{20}$ -18° in CHCl_3 (also obtained from the *l*-fucitol CPh_3 ether of Valentin, A., 1932, 42), converted by HBr-AcOH into *l*-fucitol 1-bromide 2:3:4:5-tetra-acetate (I), m.p. 142–143°, $[\alpha]_D^{20}$ -9.8° in CHCl_3 , and by H_2O in hot AcOH into *l*-fucitol 2:3:4:5-tetra-acetate, m.p. 92–94°, $[\alpha]_D^{20}$ -15° in CHCl_3 , which with HBr-AcOH gives (I) and with Ac_2O gives the penta-acetate, m.p. 127°, $[\alpha]_D^{20}$ $+20.5^\circ$ in CHCl_3 . Dulcitol and CPh_3Cl (2 mols.) in $\text{C}_5\text{H}_5\text{N}$ give the 1- CPh_3 , m.p. 83°, and 1:6-(CPh_3)₂ ether (II), m.p. 183–184°; (II) is isolated as its compound (III), $+2\text{C}_5\text{H}_5\text{N.HCl}$, m.p. 182–184°, and thence as solvate (IV), $+\text{EtOH}$, m.p. 183–184° (sinters at 80°), from which the EtOH is removed by heating at 110°/vac. over P_2O_5 . With $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at 0°, (III) or (IV) gives dulcitol 1:6-(CPh_3)₂ ether 2:3:4:5-tetra-acetate, m.p. 237–238°, which with HBr-AcOH gives the 1:6-dibromide 2:3:4:5-tetra-acetate, m.p. 197–198°. With PhCHO and ZnCl_2 , (II) gives dibenzylidenedulcitol 1:6-(CPh_3)₂ ether, m.p. 233–234°. Xylitol with CPh_3Cl , followed by Ac_2O , in $\text{C}_5\text{H}_5\text{N}$ at room temp. gives xylitol 1:5-(CPh_3)₂ ether 2:3:4-triacetate, m.p. 206°. *d*-Mannitol in $\text{C}_5\text{H}_5\text{N}$ with CPh_3Cl at 90°, followed by Ac_2O at 0°, gives *d*-mannitol 1- CPh_3 ether 2:3:4:5:6-penta-acetate, m.p. 163–164°, $[\alpha]_D^{20}$ $+35.5^\circ$ in CHCl_3 . R. S. C.

Substituted ethers derived from ethylene chlorohydrin. S. P. LINGO with H. R. HENZE (J. Amer. Chem. Soc., 1939, 61, 1574–1576; cf. A., 1939, II, 299).—Saturating a mixture of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and RCHO with HCl at $<0^\circ$ gives $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Cl}\cdot\text{CH}_2$ ether, b.p. 46°/10 mm., ($\text{CH}_2\text{Cl}\cdot\text{CH}_2$)₂ ether (prep. from par-acetaldehyde), b.p. 51°/10 mm., $\text{CH}_2\text{Cl}\cdot\text{CH}_2$ α -chloro-*n*-propyl, b.p. 60°/10 mm., and *n*-butyl ether, b.p. 71°/10 mm., all unstable, which with CuCN , $\text{Hg}(\text{CN})_2$, or AgCN (gives no carbimide) (not NaCN or KCN) in C_6H_6 yield $\text{CH}_2\cdot\text{CN}\cdot\text{CH}_2\text{Cl}\cdot\text{CH}_2$ ether, b.p. 109–110°/27.5 mm., $\text{CH}_2\text{Cl}\cdot\text{CH}_2$ α -cyano-ethyl, b.p. 91°/10 mm., *n*-propyl, b.p. 97.5°/6 mm., and *n*-butyl ether, b.p. 105.5°/4.5 mm. With MgRHal in Et_2O these give *Me* β -chloroethoxymethyl ketone, b.p. 72–73°/8 mm. (semicarbazone, m.p. 103°), β -chloroethoxymethyl *Et*, b.p. 82°/5 mm. (semicarbazone, m.p. 92.5°), *Pr*^a, b.p. 88.5–90°/4 mm., *Bu*^a, b.p. 88.2–89°/2 mm., *n*-amyl, b.p. 96.2–97°/2.5 mm., and isoamyl ketone, b.p. 99.5–100.5°/2.5 mm., *Ph* β -chloroethoxymethyl ketone, m.p. 26.1°, b.p. 152–155°/4.5 mm. (semicarbazone, m.p. 119.5–120°), *Me*, b.p. 70–72°/4 mm., and *Et* α - β' -chloroethoxyethyl ketone, b.p. 71°/3.5 mm. (semicarbazone, m.p. 104°), α - β' -chloroethoxyethyl *Pr*^a ketone, b.p. 87.5–88.3°/3 mm. (semicarbazone, m.p. 127°), and *Me* β -iodoethoxymethyl ketone, b.p. 90–92°/4 mm. 5- β -Chloroethoxymethyl-5-isoamyl-, m.p. 152.5°, 5-phenyl-5- β -chloroethoxymethyl-, m.p. 159.8°, 5-ethyl-5- α - β' -chloroethoxyethyl-, m.p. 168.8°, and 5- α - β' -chloroethoxyethyl-5-*n*-propyl-, m.p. 140.5°, hydantoin (but no other hydantoins) were also obtained. B.p. of the ketones and m.p. are corr. *n* and *d* are given.

R. S. C.

Preparation of ethyl hypochlorite. H. T. COMASTRI (Anal. Asoc. Quím. Argentina, 1939, 27, 41–44).—The instability of EtOCl is attributed to the presence of HCl . After treatment with ice-cold

dil. NaHCO_3 saturated with NaCl it will keep for several hr. F. R. G.

Sulphurous esters and chlorosulphites. P. CARRÉ and D. LIBERMANN (Bull. Soc. chim., 1939, [v], 6, 1255).—The observations of Gerrard (A., 1939, II, 97) were recorded previously by the authors (A., 1933, 696). J. W. S.

Hydrolysis of α - and β -glycerophosphates. M. C. BAILLY (Compt. rend., 1939, 208, 1820–1822).— Na α - and β -glycerophosphate are hydrolysed without isomerisation (cf. A., 1939, I, 205) by boiling H_2SO_4 at p_H 3.62, the β - twice as rapidly as the α -form. Below p_H 3 isomerisation accompanies hydrolysis. J. L. D.

X-Ray and thermal examination of the glycerides. VI. Symmetrical mixed triglycerides $\text{CH}(\text{O}\cdot\text{CO}\cdot\text{R}')(\text{CH}_2\cdot\text{O}\cdot\text{COR})_2$ (continued). T. MALKIN and M. L. MEARA (J.C.S., 1939, 1141–1144).—The following symmetrical triglycerides have been prepared by the methods used previously (A., 1939, II, 97), and all exist in four solid modifications, vitreous, α , β' , and β , the m.p. of which are in the order given: β -decodimyrustin (16°, 37°, 40°, 43.5°), β -laurodipalmitin (34°, 47°, 50°, 53.5°), β -myristodistearin (47°, 56°, 59°, 62.5°), β -myristodidecain (3°, 21°, 30°, 34°), β -palmitodilaurin (I) (19°, 35°, 42.5°, 45.5°), β -stearodimyrustin (II) (33°, 47°, 53°, 55.5°), β -decodipalmitin (20°, 42°, 48°, 51.5°), β -laurodistearin (36°, 52°, 58°, 60.5°), β -palmitodidecain (6°, 27°, 36°, 40°), β -stearodilaurin (21°, 38°, 43°, 47°), β -stearodidecain (5°, 34°, 40°, 44.5°), and β -decodistearin (30°, 47°, 53°, 57°). In contrast to other glycerides, the long spacings of the β forms of all except (I) and (II) correspond with twice the length of a single mol., but the side spacings do not suggest any fundamental difference in structure. J. D. R.

Autoxidation of organic sulphur compounds. M. DELÉPINE (Bull. Soc. chim., 1939, [v], 6, 1234–1236; cf. A., 1922, i, 914).—The results obtained (*loc. cit.*) are confirmed, i.e., that action ceases very soon, with a permanent arrest in autoxidation. Experiments performed in 1912, with S compounds, e.g., OMe-CS-SMe , MeCS-OEt , in air or O_2 , are further examined; after 26 years in the tubes, similar results are obtained. A. T. P.

Structural identity of polysulphones prepared by peroxide catalysis and under the influence of ultra-violet light. C. S. MARVEL and W. H. SHARKEY (J. Amer. Chem. Soc., 1939, 61, 1603).—On irradiation with ultra-violet light for ~ 1 week Δ^a -pentene combines with SO_2 ; the polysulphone formed in this way is identical with that formed in presence of peroxide catalysts. W. R. A.

***pp'*-Diaminodiphenylmethane as a reagent for the identification of monobasic, saturated, aliphatic acids.** A. W. RALSTON and M. R. MCCORCKLE (J. Amer. Chem. Soc., 1939, 61, 1604–1605).—($p\text{-NH}_2\cdot\text{C}_6\text{H}_4$)₂ CH_2 and RCO_2H , when heated to boiling, give *pp'*-di(acet-, m.p. 227–228°, -di(propion-, m.p. 212–213°, -di(*n*-butyr-, m.p. 197–198°, -di(*n*-valer-, m.p. 188–189°, -di(*n*-hex-, m.p. 185–186°,

-*di*-(*n*-*hept*-, m.p. 183—184°, -*di*-(*n*-*oct*-, m.p. 182—183°, -*di*-(*n*-*non*-, m.p. 176—177°, -*di*-(*n*-*dec*-, m.p. 178—179°, -*di*-(*n*-*undec*-, m.p. 175—176°, -*di*-(*laur*-, m.p. 174—175°, -*di*-(*n*-*tridec*-, m.p. 172—173°, -*di*-(*myrist*-, m.p. 170—171°, -*di*-(*n*-*pentadec*-, m.p. 167—168°, -*di*-(*palmit*-, m.p. 167—168°, -*di*-(*margar*-, m.p. 164—165°, and -*di*-(*stear*-, m.p. 164—165°, -*amido*)*di*phenylmethane, which are useful for characterising the acids. The lower members give good depressions of the m.p. when mixed. R. S. C.

Xanthates of metals of group VI. L. MALATESTA (Gazzetta, 1939, 69, 408—416).—(NH_4)₂MoO₄ and OEt·CS₂·K treated in H₂O with SO₂ give molybdenyl tetraethylxanthate, new m.p. 118.5° (slight decomp.) (cf. Montequi, A., 1930, 1028) (3C₂H₅N additive product), which with aq. KCN in COMe₂ gives Mo₂O₃(CN)₄·4H₂O and KCS₂·OEt; with solid KCN in COMe₂, K molybdocyanides are formed. *Molybdenyl tetra-methyl*-, decomp. 100—120°, -*n-propyl*-, m.p. 89—91° (slight decomp.), -*isopropyl*-, m.p. 114°, -*n-butyl*-, m.p. 75°, -*isobutyl*-, m.p. 106—107.5° (slight decomp.), -*isoamyl*-, m.p. 105° (decomp.), and -*cyclohexyl-xanthate*, m.p. 121° (decomp.), are prepared similarly. UO₂(NO₃)₂ and OR·CS₂·K give *uranyl di-methyl*-, -*ethyl*-, (easily hydrolysed), -*isoamyl*-, and -*isopropyl-xanthate*, and similar products, all of which decompose at 50—60°. Similar derivatives of W are not obtained. E. W. W.

Preparation of acrylic acid esters. P. P. KOBKO, M. M. KOTON, and F. S. FLORINSKI (J. Appl. Chem. Russ., 1939, 12, 313—316).—Esters of CH₂:CH·CO₂H are prepared as follows: CH₂:CH·CHO (+ Br) → CH₂Br·CHBr·CHO (+ HNO₃) → CH₂Br·CHBr·CO₂H (+ ROH) → CH₂Br·CHBr·CO₂R (+ Zn) → CH₂:CH·CO₂R (R = Bu, *isoamyl*). R. T.

Preparation of derivatives of the higher fatty acids. E. OCHIAI and M. SHIMIZU (J. Pharm. Soc. Japan, 1938, 58, 302—303).—An attempt to prepare derivatives of stearic acid having p_H 5—8 in aq. solution. The following are described: *stearylquinine* (Pt salt, m.p. 217° decomp.; *hydrochloride*, m.p. 69°, p_H 2.5), *stearyltropine*, m.p. 49.8° (*picrate*, m.p. 96.8°; *perchlorate*, m.p. 94.5°; *hydrochloride*, m.p. 144°, p_H 4.3), *heptadecylamine hydrochloride*, p_H 4.8, *stearhydrazide*, m.p. 114°. S. H. H.

Lipins of tubercle bacilli. LVII. Mycolic acids of avian tubercle bacillus wax. R. J. ANDERSON and M. M. CREIGHTON (J. Biol. Chem., 1939, 129, 57—63).— α - (I), C₃₈H₇₄O₃, m.p. 69—70°, $[\alpha]_D^{25} +5.6^\circ$ in CHCl₃ (*Br*-derivative, 22.4% Br, m.p. 47—49°), and β - (II), C₃₈H₇₄O₃, m.p. 60—61°, $[\alpha]_D^{25} +5.5^\circ$ in CHCl₃ (*Br*-derivative, 22.9% Br, m.p. 43—49°), -*mycolic acid* have been obtained from the avian tubercle bacillus wax. These acids differ from the corresponding acids from human tubercle bacilli in not containing OMe-groups. (I) decomposes on heating at 1 mm. to form a branched-chain pentacosanoic acid, C₂₅H₅₀O₂, m.p. 78—79°, in 25% yield, whereas (II) similarly yields *n*-tetracosanoic acid (21%). The non-volatile residues from (I) and (II) are separable into highly unsaturated fractions of varying solubility in Et₂O and mol. wt. 1000—1100 (Rast). P. G. M.

Resonance reaction. II. P. NEOGI and K. L. MONDAL (J. Indian Chem. Soc., 1939, 16, 239—240).—Maleic acid is converted into fumaric and citraconic into mesaconic in presence of MnO₂ by a "resonance reaction" (A., 1930, 550). W. R. A.

***cis-trans*-Isomerisation with boron fluoride.** C. C. PRICE and M. MEISTER (J. Amer. Chem. Soc., 1939, 61, 1595—1597).—BF₃ in CCl₄ or BF₃·Et₂O equilibrates *cis*- and *trans*-stilbene (93.1% of *trans*), probably by forming a complex, ⁺CHPh·CHPh→BF₃[−] (cf. Price *et al.*, A., 1938, II, 478). AlCl₃ in the Friedel-Crafts reaction and H⁺ in the isomerisation of olefines form similar complexes. Et₂ maleate is unaffected by BF₃, probably because the latter forms complexes with the CO₂Et rather than with the C:C. R. S. C.

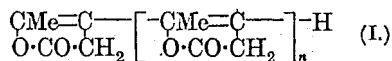
Hydroxylation of unsaturated substances. V. Catalytic hydroxylation of unsaturated substances with functional groups. N. A. MILAS, S. SUSSMAN, and H. S. MASON (J. Amer. Chem. Soc., 1939, 61, 1845—1847; cf. A., 1938, II, 1).—H₂O₂·Bu^oOH·OsO₄ converts Et crotonate into Me·[CH(OH)]₂·CO₂Et (56%), Et₂ maleate into Et₂ mesotartrate (41%), Et₂ fumarate into Et₂ *r*-tartrate (58%), mesityl oxide into β -methyl-*n*-pentane- γ -diol- δ -one (23%), b.p. 104—110°/16 mm. [*p*-nitrophenylhydrazine, m.p. 251—253° (decomp.)], CH₃:CH·OAc, (CH₃:CH)₂O, or CH₃:CHBr into OH·CH₂:CHO (60, 96, 12.5%), and oleic acid into κ -dihydroxystearic acid. CHPh:CH·CH₂:OH gives 12.2% of OH·CHPh·CH(OH)·CH₂:OH (I), an ether of (I), C₁₈H₃₂O₅, m.p. 155.5—156° (*tetrabenzoate*, m.p. 118—119°), and (?) another ether (*tetrabenzoate*, m.p. 217°), but is mostly converted into PhCHO and OH·CH₂:CHO. R. S. C.

M.p. curve of esters of the dihydroxystearic acid from castor oil. S. ISHIKAWA and E. KURODA (Sci. Rep. Tokyo Bunrika Daigaku, 1939, 3, 265—271).—Me θ -dihydrostearate, m.p. 110° (corr., Berl), is hydrolysed and the acid is esterified by the requisite alcohol and PhSO₂Cl to the *Et*, m.p. 106°, *Pr*^a, m.p. 100.6°, *Bu*^a, m.p. 93.0°, *n*-*amyl*, m.p. 93.7°, *n*-*hexyl*, m.p. 92.2°, *n*-*heptyl*, m.p. 94.3°, *n*-*octyl*, m.p. 93.4°, *n*-*nonyl*, m.p. 95.4°, *n*-*decyl*, m.p. 94.9°, *n*-*dodecyl*, m.p. 95.6°, *n*-*tetradecyl*, m.p. 96.6°, *n*-*hexadecyl*, m.p. 97.4°, and *n*-*octadecyl*, m.p. 98.2°, ester. H. W.

Synthesis of *n*-eicosanedicarboxylic acid, CO₂H·[CH₂]₂₀·CO₂H, and *n*-docosanedicarboxylic acid, CO₂H·[CH₂]₂₂·CO₂H. S. SHINA (J. Soc. Chem. Ind. Japan, 1939, 42, 147B; cf. A., 1937, II, 483).—CO₂Et·[CH₂]₁₈·CO₂Et is converted via the glycol, di-iodide, and dicyanide into CO₂H·[CH₂]₂₀·CO₂H, m.p. 126.9—127.1° (Me₂, m.p. 71—71.2°, and Et₂ ester, m.p. 61—61.2°), which by similar reactions yields the glycol, m.p. 105.3—105.5°, di-iodide, m.p. 71.9—72.1°, and CO₂H·[CH₂]₂₂·CO₂H, m.p. 126.9—127.1° (Me₂, m.p. 75.0—75.2°, and Et₂ ester, m.p. 65.9—66.1°). A. LI.

Structure of vinyl polymerides. III. Polymeride from α -angelicalactone. C. S. MARVEL and C. L. LEVESQUE (J. Amer. Chem. Soc., 1939, 61, 1682—1684; cf. A., 1938, II, 255).—BF₃·Et₂O (0.4

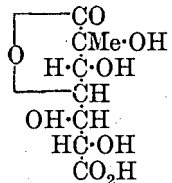
c.c.) (but not peroxides) in CS_2 (40 c.c.) converts α -angelicalactone (15 g.) into a *polymeride* (I), in which



n is 7—8 as judged by the mol. wt. in COPh_2 and titration of residual C:C by Br in CCl_4 . 75% of the lactone groups appear from the following evidence to be retained. (I) dissolves slowly in aq. NaOH and undergoes 84% reaction with NH_3 -dioxan at 150—160° to give a lactam and ~90% reaction with LiPh to give a polyalcohol. Since BF_3 is a *trans*-esterifying reagent, some of the $\text{CH}_2\text{CO}_2\text{H}$ are expected to become isolated and the above reactions are consistent with the head-to-tail structure of (I). In presence of Cu chromite at 250°/400 atm., (I) absorbs twice the calc. amount of H_2 and gives only 70% of polymeric product, this having a lower mol. wt.; the reaction is explained on the basis of (I) as due to fission of C:O linkings in $\text{O} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{O}$ leading to some units of types $\cdot \text{CHMe} \cdot \text{CH}(\text{CH}_2\text{CO}_2\text{H}) \cdot$ and $\cdot \text{CHMe} \cdot \text{CH}(\text{CH}_2\text{CH}_2\text{OH}) \cdot$. Hydrogenation at 175°/400 atm. leads to absorption of 0.84 ± 0.05 mol. of H_2 , which agrees with the val. (0.75) calc. by statistical analysis (Flory, A., 1939, II, 401) for C:O fission allowing C:O linkings to become isolated; little C:C cleavage occurred at this temp. Isomerisation to β -angelicalactone prior to polymerisation would give structures not containing $\text{O} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{O}$ and is thus excluded. Ultra-violet light gives a more mobile *polymeride* of lower mol. wt. R. S. C.

Reduction of *dl*-erythronolactone to *dl*-erythrose. J. W. E. GLATTFELD and B. D. KRIBBEN (J. Amer. Chem. Soc., 1939, 61, 1720—1725).—*dl*-Erythronolactone with Ac_2O -HCl or AcCl gives the *lactone diacetate*, m.p. 52.5—53°, and with KOH or NaOH in MeOH gives *K* or *Na dl*-erythronate. The *K* salt with AcCl gives *dl*-erythronic acid triacetate (74%), an oil (*Ca* salt), which with SOCl_2 (must be pure) gives the *acid chloride*, b.p. 114—116°/2 mm. H_2 -Pd-BaSO₄ in xylene reduces and partly deacetylates this, giving *dl*-erythrose diacetate (I) (20%), b.p. 126—129°/2 mm. Hydrolysis of (I) gives *dl*-erythrose (identified as phenyllosazone), but $2 : 4 \cdot (\text{NO}_2)_2\text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{NH}_2$ gives a *substance* (? the *diacetyltriazine*), m.p. 172—173°. R. S. C.

Tetrahydroxyadipic acid. O. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1939, 11, 266—271).—Ba δ -ketorhamnohexonate and aq. HCN give a *lactonic acid* (I), $\text{C}_8\text{H}_{12}\text{O}_8$, m.p. 198°, $[\alpha]_D -25.4^\circ$ (and an oily epimeride), which gives the *Ba* salt, $\text{C}_8\text{H}_{12}\text{O}_8\text{Ba} \cdot 2\text{H}_2\text{O}$, and by the usual methods an oily methylheptose, which yields a trace of an osazone. Distillation of (I) gives a pyrone. These facts and Hudson's rule indicate the formula shown for (I). R. S. C.



Relations between rotatory power and structure in the sugar group. XXXII. Rotations of the aldonic γ -lactones. C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1525—1528; cf. A., 1939, II, 300).—The rule of optical superposition applies to

γ -aldolactones if they are divided into classes of the (A) ribose-aldonic and (B) xylonic-lyxonic pairs of epimerides. Data for class B are, however, scanty. This principle is not always in accord with the qual. lactone rule. It shows *D*-gulo-*L*-talohexolactone to belong to class A. $[\alpha]$ of several unknown hepto- and octo-lactones are calc. *L*-Epirhamno- and β -*L*-fucohexolactone are probably δ -lactones (speed of mutarotation). *D*-Gluco-*D*-idoheptolactone behaves abnormally in solution. R. S. C.

Preparation of mannonolactones from seeds of date palm (*Phoenix dactylifera*). Effect on gastric mucin smears. K. J. GOLDNER and C. H. ROGERS (J. Amer. Pharm. Assoc., 1939, 28, 364—369).—The seeds contain 48.85% of mannan and 0.68% of galactan. The prep. from *Ca* mannonate of δ -, m.p. 159—165°, $[\alpha]_D^{20} +114.2^\circ$ to $+41.3^\circ$ in H_2O (14 days), and γ -lactone, m.p. 151°, $[\alpha]_D^{20} +51.0^\circ$ in H_2O , *Me*, m.p. 155°, *Et*, m.p. 161°, *Pr*^B, m.p. 169°, and *Bu*^a mannonate, m.p. 144°, and mannoethanolamide, m.p. 149—150°, $[\alpha]_D^{20} -14.4^\circ$ in H_2O , is described. The efficiency of these substances in dissolving mucin and their non-toxicity indicate their applicability to dental cleaning preps. F. O. H.

Isolation of ketouronic acids as crystalline alkaloidal salts. J. P. HART and M. R. EVERETT (J. Amer. Chem. Soc., 1939, 61, 1822—1824).—1% aq. solutions of sugars are oxidised by Br at ~25°; after removal of the Br and HBr, the ketouronic acids are isolated as *Ba* salts and crystallised as *brucine* salts. *Brucine* 1- (I) (from *d*-gulolactone), m.p. 165—166°, $[\alpha]_D^{25} -24.5^\circ$, and *d*-fructo-6-uronate (from *d*-mannose), m.p. 192—192.5° (decomp.), $[\alpha]_D^{25} -15.5^\circ$, 1-*tagato*-6-uronate (from *d*-galactose), m.p. 189—189.5° (decomp.), $[\alpha]_D^{25} -17^\circ$, *d*-xyloketouronate (from *d*-xylose), m.p. 168—169°, $[\alpha]_D^{25} -9^\circ$, *l*-sorbo-6-uronate (from *d*-glucose), m.p. (anhyd.) 174—175° (decomp.) and (+2H₂O) 182° (decomp.), $[\alpha]_D^{25} -24^\circ$, and 1-deoxy-*l*-fructo-6-uronate [with (I) from *l*-rhamnose], m.p. 128—129°, $[\alpha]_D^{25} -32^\circ$ (all in H_2O), are thus obtained. The ketose structure of the acids is shown by their stability to Br. Naphthoresorcinol, orcinol, and Molisch tests of the salts are identical. R. S. C.

New water-soluble calcium salt, calcium gluconate-glucoheptonate. A. SALOMON (Pharm. Weekblad, 1939, 76, 914—917).—*Ca* gluconate-glucoheptonate, prepared by mixing solutions of *Ca* gluconate and *Ca* glucoheptonate or by neutralising a solution of the two acids with $\text{Ca}(\text{OH})_2$, is very sol. in H_2O (50%) and 11.5% solutions ($p_H \sim 7$) are suitable for intravenous injection. S. C.

Structure of alginic acid. E. L. HIRST, J. K. N. JONES, and (Miss) W. O. JONES (Nature, 1939, 143, 857).—High yields of *d*-mannuronic acid (I) are obtained by the action of MeOH -HCl on alginic acid (II). A partly degraded form of (II) of comparatively low mol. wt. has been isolated by means of the same reagent. With TIOEt and MeI it gives the corresponding fully methylated derivative, which, on hydrolysis (conc. HNO_3) and degradative oxidation, yields mesodimethoxysuccinic acid (III), indicating that in each of the (I) residues the *Me* groups were

attached at C₁₂ and C₁₃. This was confirmed as follows. Methylated (II) with MeOH-HCl under pressure gives the Me ester of 2 : 3-dimethylmannuronide, which on hydrolysis and oxidation (aq. Br) yields 2 : 3-dimethylmannosaccharic acid, which is oxidised by HIO₄ to CHO·CO₂H and the semi-aldehyde of (III). (II) appears to be composed of *d*-mannuronic anhydride residues linked glycosidically. In addition, (II) contains a chain of (I) residues in each of which the OH at C₁₂ and C₁₃ are free. The glycosidic linkage is either 1 : 5 or (probably) 1 : 4. Structural resemblances with cellulose and pectic acid are pointed out. L. S. T.

Condensation of acetaldehyde and vinyl acetate. C. S. MARVEL, J. HARMON, and E. H. RIDDLE (J. Org. Chem., 1939, 4, 252—255).—Successive addition of Na and vinyl acetate (I) to MeCHO gives $\alpha\gamma$ -ethylidenedioxybutyl acetate, b.p. 74—75°/6 mm. Under similar conditions (I) does not react with EtCHO, PrⁿCHO, PrⁱCHO, or PhCHO. Reaction between MeCHO and (I) does not occur in presence of KOH-EtOH, ZnCl₂, Ba(OH)₂, Mg(OMe)₂, NaOEt, NaOPh, anhyd. Na₂CO₃, SnCl₄, AcOH + *p*-C₆H₄Me·SO₃H, dry HCl, or dry *p*-C₆H₄Me·SO₃H in C₆H₆. H. W.

Synthesis of acetals of chloro- and bromoacetaldehyde. E. M. FILACHIONE (J. Amer. Chem. Soc., 1939, 61, 1705—1706).—Passage of Cl₂ into CH₂:CH·OAc in abs. EtOH or MeOH cooled in COMe₂-CO₂ gives Et₂ (83%), b.p. 53—54°/16 mm., or Me₂ chloroacetal (53%), b.p. 124.5—126.5°. At -10° air carrying Br gives Et₂ bromoacetal (68%), b.p. 62—63°/15 mm.; CHCl₃-Br, added to the MeOH solution at -40°, gives 46% of Me₂ bromoacetal, b.p. 48—51°/18 mm. Structures are proved by hydrolysis, identification of MeOH or EtOH, and oxidation (H₂O₂) of the aldehyde to the acid. R. S. C.

Aldehydic perfumes. II. Synthesis of pelargonaldehyde. S. ISHIKAWA and A. MIYATA (Sci. Rep. Tokyo Bunrika Daigaku, 1939, 3, 257—263).—The yield of pelargonaldehyde (I) obtained by ozonisation of oleic acid suspended in aq. NaHSO₃ with a little decahydronaphthalene as dispersing agent does not exceed 20%. Oxidation of Me 9:1-dihydroxystearate (II) with Pb(OAc)₄ in AcOH gives (I) in 50% yield accompanied by Me γ -aldehydo-octoate (2 : 4-dinitrophenylhydrazone, m.p. 67—68°). (I) is also obtained in very modest yield by heating (II) with sand at 650° in CO₂. H. W.

C₁₀, C₁₂, and C₁₄ aldehydes from copra oil. R. ESCOURROU (Bull. Soc. chim., 1939, [v], 6, 1173—1181).—Fatty acids (obtained by saponification of the oil) and PCl₃ give the corresponding chlorides, hydrogenated (Pt) under reduced pressure (not at atm.) to the aldehydes. Lauryl chloride, b.p. 141°/14 mm., at 300—320°/170—180 mm., affords undecane, b.p. 194—195°/760 mm.; at 200—205°/50 mm., lauraldehyde is formed, with some tricosane, C₂₃H₄₈ (mechanism of formation discussed). The use of Raney Ni at 160°/50 or 580 mm. gives no aldehyde. Hydrogenation (Pt) of myristyl chloride, b.p. 195°/45—47 mm., at 220—230°/60—65 mm. affords Me·[CH₂]₁₂·CHO and tridecane, C₁₃H₂₈. Decoyl

chloride, b.p. 115°/13 mm., at 200°/80—90 mm. gives decaldehyde, b.p. 207—210°/760 mm., and polymerised products. Octoyl chloride, b.p. 75—77°/8—10 mm., at 195°/80—90 mm. gives octaldehyde, b.p. 72°/20 mm., with some polymerisation. A. T. P.

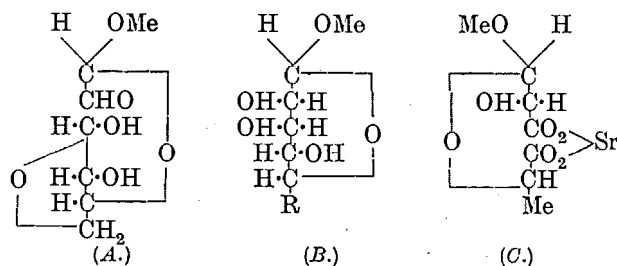
Reaction of methyl α -chloroethyl ketone with potassium cyanide. R. JUSTONI (Gazzetta, 1939, 69, 378—391).—The product from COMe·CHMeCl (I) and aq. KCN is not COMe·CHMe·CN (cf. Henry *et al.*, A., 1900, i, 537), nor a dimethylisooxazole (II) (cf. Youtz *et al.*, A., 1930, 93), but $\alpha\beta$ -oxido- α -methylbutyronitrile, $\begin{array}{c} \text{CHMe} \\ | \\ \text{O} \end{array} \text{---} \text{CMe} \cdot \text{CN}$, (III), b.p. 145°/755 mm. With *p*-NO₂·C₆H₄·NH·NH₂, (II) does not react, but (III) gives (*p*-NO₂·C₆H₄·NH·N·CMe)₂ (and similarly other derivatives of Ac₂). In EtOH, (I) and KCN also give (III), with CHMeAc·CN [which is, however, not obtained from (III) and Na or NaOEt (cf. *loc. cit.*)]. With liquid HCN, (I) gives Me α -chloroethyl ketone cyanohydrin, b.p. 120—123°/15 mm., which with aq. KOH yields (III), with a very small proportion of (I). With KOH-MeOH, (I) yields acetoin, of which the cyanohydrin, b.p. 120—123°/15—16 mm., with H₂SO₄ or P₂O₅ gives only slight traces of (III). E. W. W.

Keto-ethers. V. β -Chloroisopropoxymethyl ketones derived from propylene chlorohydrin. J. J. SPURLOCK and H. R. HENZE (J. Org. Chem., 1939, 4, 234—241).—CH₂Cl·O·CMe₂Cl (I), b.p. 106—107°/146 mm., 160—161°/747 mm., is obtained by saturating OH·CHMe·CH₂Cl and 36% CH₂O with HCl at 0° or from BzCl and OH·CHMe·CH₂Cl at 145—155°. It is best converted into β -chloroisopropoxyacetoneitrile (II), b.p. 98—99° (corr.)/15 mm., by treatment with CuCN in PhMe at 120° with purification by distillation in vac. Alternatively, propylene $\alpha\beta$ -oxide is saturated with HCl and treated with CH₂O and again saturated with HCl, giving di-(β -chloroisopropyl) formal, b.p. 112.5—113.5°/11 mm., which is treated with BzCl, thereby yielding β -chloroisopropyl benzoate, b.p. 106—107°/2—3 mm., and (I), which is then treated with CuCN. Poorer yields of (II) are derived from (I) and Hg(CN)₂ in boiling C₆H₆, whereas (I) and KCN scarcely react. Crude (II) is transformed by EtOH and HCl into Et β -chloroisopropoxyacetate, b.p. 110—111°/19 mm., converted by conc. aq. NH₃ into β -chloroisopropoxyacetamide, m.p. 31.2° (corr.), which is dehydrated by P₂O₅ at 130° to (II), b.p. 104—105°/20 mm. (II) is transformed by the appropriate Grignard reagent into the following β -chloroisopropoxymethyl ketones; Me, b.p. 73—74°/4 mm.; Et, 77—78°/4 mm.; Pr, m.p. 95—96°/6 mm.; Bu, b.p. 101—102°/3 mm.; amyl, b.p. 109—110°/3 mm.; Ph, b.p. 135—136°/3 mm.; CH₂Ph, b.p. 151—152°/4 mm. All b.p. are corr. The corresponding 2 : 4-dinitrophenylhydrazones have m.p. 120.5—121.5°, 85.5—86.5°, 80.5—81.0°, 69—69.5°, 91.5—92.5°, 181—182°, and 77—78° (corr.), respectively. The mol. refraction of these ketones is a better index of purity than is the parachor. H. W.

Stability of a higher ketone and a higher secondary alcohol towards heat. K. KINO (J. Soc. Chem. Ind. Japan, 1939, 42, 187B).—Stearone (from commercial stearic acid), and the corresponding

carbinol (Na + BuOH), were heated at various temp., and the colour, m.p., mol. wt., and OH val. (after reduction in the former case) of the products recorded. Little decomp. occurs below 260°. A. LI.

Oxidation of glucosides by lead tetra-acetate. R. C. HOCKETT and W. S. MCCLENAHAN (J. Amer. Chem. Soc., 1939, 61, 1667—1671).—*cis*-Glycols of the sugar series are always attacked faster than are the *trans*-glycols by Pb(OAc)₄ (6.5 mols., equiv. to infinite excess since 13 mols. react no faster); 21 examples are cited. If the ether-aldehyde formed can yield a *cis*-glycol of type (A) by cyclic acetal formation, a second mol. of Pb(OAc)₄ is very rapidly consumed; if this is impossible, reaction slows down after 1 mol. has been used; examples are α -methyl-*D*-mannopyranoside (B) (R = CH₂·OH), which gives (A), and α -methyl-*L*-rhamnopyranoside (B) (R = Me) and α -



methyl-*D*-mannopyranoside 6-CPh₃ ether (B) (R = CH₂·O·CPh₃), which cannot give (A). α -Methyl-*L*-fucoside gives the *Sr* salt (C), +2H₂O, $[\alpha]_D^{20} +29.8^\circ$ in H₂O. R. S. C.

Behaviour of glucose dimethyl acetal towards carbohydrases. N. K. RICHTMYER, M. ADAMS, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1833—1834).—Glucose Me₂ acetal is unaffected by top yeast, taka-diastase, emulsin, maltase, invertase, pancreatic or malt amylase. R. S. C.

Glucufuranosides and thioglucufuranosides. V. Hydrolysis of α -ethylthioglucufuranoside. E. PACSU and E. J. WILSON, jun. (J. Amer. Chem. Soc., 1939, 61, 1450—1454; cf. A., 1938, II, 473).—Hydrolysis of α -ethylthioglucufuranoside (improved prep.; tetra-acetate, $[\alpha]_D +150.0^\circ$ in CHCl₃) by 0.01N-HCl at 98—100° gives about 50% of glucose and EtSH, partly directly and partly by way of β -ethylthioglucufuranoside, a syrup, $[\alpha]_D^{20} -104^\circ$ in H₂O (tetra-acetate, a syrup, $[\alpha]_D^{20} -53.1^\circ$ in CHCl₃), but much rearrangement to α - (I), $[\alpha]_D^{20} +261.4^\circ$ in H₂O (tetra-acetate, m.p. 95°, $[\alpha]_D^{20} +194.1^\circ$ in CHCl₃), and β -ethylthioglucopyranoside, a syrup, $[\alpha]_D -60^\circ$ (tetra-acetate, $[\alpha]_D -25.6^\circ$ in CHCl₃), also occurs. The principle of optical superposition does not apply to (I). Glucose Et mercaptal has $[\alpha]_D^{20} -37.4^\circ$ in H₂O. R. S. C.

Behaviour of the dimethyl acetals of glucose and galactose under hydrolytic and glucoside-forming conditions. M. L. WOLFROM and S. W. WAISBROT (J. Amer. Chem. Soc., 1939, 61, 1408—1411).—Complex changes of $[\alpha]$ of *D*-glucose and *D*-galactose Me₂ acetals with 0.05% HCl in MeOH or H₂O at 25° and determination of readily hydrolysable material during the reaction show that the very rapid

initial hydrolysis is followed by formation of unstable non-pyranoid glucosides, which later slowly give the stable pyranosides. R. S. C.

Synthetic galactose 1-phosphate. H. W. KOSTERLITZ (Biochem. J., 1939, 33, 1087—1093; cf. A., 1938, III, 933).—Tri(tetra-acetylgalactose) 1-phosphate, $[\alpha]_D^{17} +119.9^\circ$ in MeOH (from acetobromogalactose and Ag₃PO₄), with MeOH-HCl at 25° for 8 hr. yields galactose 1-phosphate, which was isolated as the crude Ba and dibrucine salts; the latter afforded the K₂ salt (+2H₂O), $[\alpha]_D^{18} +108.2^\circ$ in H₂O (anhyd. salt), which was converted into the Ba salt, $[\alpha]_D^{18} +92.7^\circ$. The ester appears to be α -galactopyranose 1-phosphate. F. O. H.

Glucufuranosides and thioglucufuranosides. VI. Preparation of dimethyl acetal and methylfuranosides from *D*-fructose diethyl mercaptal. E. PACSU (J. Amer. Chem. Soc., 1939, 61, 1671—1675; cf. A., 1938, II, 432, also above).—*D*-Fructose Et₂ mercaptal (prep. from the penta-acetate modified to give a quant. yield) with HgCl₂-HgO in MeOH at -80° gives only *D*-fructose Me₂ acetal (I), m.p. 107—108°, $[\alpha]_D^{20} -45.6^\circ$, -63.0°, $[\alpha]_{563}^{20} -35.6^\circ$, -50.0°, $[\alpha]_{563}^{18} -53.6^\circ$, -76.1° in H₂O and MeOH, respectively (penta-acetate, m.p. 109°, $[\alpha]_D^{20} 0$ in CHCl₃), but at room temp. gives also the cryst. and syrupy γ -methylfructosides of Purves and Hudson (A., 1934, 513). Invertase at p_H 4.5 and yeast at p_H 7 are without effect on (I), but yeast in unbuffered solution ferments it owing to prior hydrolysis by the acids of the yeast; (I) is extremely sensitive to acid. Acetal and pyranoside formation from mercaptals may be independent reactions, or both may proceed by way of an intermediate of type, $>C(OR) \cdot SR$. R. S. C.

Formation of α -ethylthioglucopyranoside from glucose ethyl mercaptal. E. PACSU and E. J. WILSON, jun. (J. Amer. Chem. Soc., 1939, 61, 1930—1931).—Glucose Et₂ mercaptal and 22% HCl give α -ethylthioglucopyranoside (<20% yield) without addition of glucose (cf. Brigl *et al.*, A., 1939, II, 299). The same product (15%) is obtained from glucose and EtSH in 22% HCl. The β -pyranoside is probably also formed. R. S. C.

Action of triphenylmethyl chloride on α -methyl-*D*-mannopyranoside. A. J. WATERS, R. C. HOCKETT, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1528—1530).— α -Methyl-*D*-mannopyranoside is etherified preferentially at the primary OH by CPh₃Cl in C₅H₅N, giving the 6-CPh₃ ether, +C₅H₅N, m.p. 101—102°, $[\alpha]_D^{20} +23.45^\circ$ in CHCl₃ (CaCl₂ compound, +2.5EtOH, m.p. ~110—112°, $[\alpha]_D^{20} +26.6^\circ$ in MeOH), the structure of which is proved as follows. With Ac₂O-C₅H₅N at 0° it gives α -methyl-*D*-mannopyranoside 6-CPh₃ ether 2:3:4-triacetate, m.p. 130°, $[\alpha]_D^{20} +44.33^\circ$ in CHCl₃, hydrolysed by cold HBr-AcOH to α -methyl-*D*-mannopyranoside 2:3:4-triacetate, m.p. 98°, $[\alpha]_D^{20} +55.54^\circ$ in CHCl₃, which with MeI-Ag₂O (5 treatments) gives a syrupy 6-Me ether. Hot 2% HCl converts this into 6-methyl-*D*-mannose, $[\alpha]_D^{20} +15.3^\circ$ in CHCl₃ [osazone = 6-methylglucosazone, m.p. 172° (lit., 177°), $[\alpha]_D^{20} -68.6^\circ \rightarrow -48.0^\circ$ in EtOH in 48 hr.]. M.p. are corr. R. S. C.

Relations between rotatory power and structure in the sugar group. XXXIII. α - and β -Methylpyranosides of *L*-fucose (*L*-galactomethyl-ose) and their triacetates. R. C. HOCKETT, F. P. PHELPS, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1658—1660; cf. A., 1939, II, 405).—The calc. $[\alpha]$ of α -methyl-*L*-fucoside (I) (Hudson, A., 1925, i, 233) is confirmed by experiment (cf. Tadokoro *et al.*, J. Biochem. Japan, 1923, 2, 461; Minsas, A., 1932, 723). *L*-Fucose (prep. from *Ascophyllum nodosum* described) and hot 1% HCl-MeOH give α -, m.p. 154°, $[\alpha]_D^{20}$ -19.7° (triacetate, m.p. 67°, $[\alpha]_D^{20}$ -149.7° in CHCl_3), and β -methyl-*L*-fucoside, m.p. 121—123°, $[\alpha]_D^{20}$ $+14.2^\circ$ in H_2O (triacetate, m.p. 96—97°, $[\alpha]_D^{20}$ $+7.1^\circ$ in CHCl_3). R. S. C.

Cleavage of the carbon chains of some methyl-aldohexomethylpyranosides by oxidation with periodic acid. W. D. MACLAY, R. M. HANN, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1660—1666).—Accepted structures are confirmed. α -Methyl-*L*-galactomethylpyranoside (Votoček's nomenclature) and HIO_4 afford *L*'-methoxy-*L*-methylglycolaldehyde, $+ \text{H}_2\text{O}$, m.p. 98—99.5°, $[\alpha]_D^{20}$ -141.4° (cf. Jackson *et al.*, A., 1937, II, 325), converted by Br-SrCO_3 into *Sr L*'-methoxy-*L*-methylglycollate (I), $+ \text{xH}_2\text{O}$, $[\alpha]_D^{20}$ (anhyd.) $+68.2^\circ$. α -Methyl-*D*-gluco-, $[\alpha]_D^{20}$ $+152.7^\circ$, β -methyl-*L*-galacto-, and β -methyl-*D*-gluco-methylpyranoside give similarly *D*'-methoxy-*D*-methyl-, m.p. 98—99°, $[\alpha]_D^{20}$ $+141.4^\circ$, *D*'-methoxy-*L*-methyl-, m.p. 100—101°, $[\alpha]_D^{20}$ $+88.8^\circ$, and *L*'-methoxy-*D*-methyl-glycolaldehyde, m.p. 101—102°, $[\alpha]_D^{20}$ -88.8° , respectively, and thence the corresponding *Sr* salts, (II), $+ \text{xH}_2\text{O}$, $[\alpha]_D^{20}$ -68.2° , (III), $[\alpha]_D^{20}$ -45.6° , and (IV), $[\alpha]_D^{20}$ $+45.7^\circ$. Hydrolysis of (I) and (III) yields $\text{H}_2\text{C}_2\text{O}_4$ and *L*-lactic acid (V), dextrorotatory (Zn salt, $+2\text{H}_2\text{O}$, $[\alpha]_D^{20}$ -7.7° to -7.9°); that of (II) and (IV) gives $\text{H}_2\text{C}_2\text{O}_4$ and *D*-lactic acid (Zn salt, prepared also from morphine *D*-lactate). Changes of $[\alpha]$ during HIO_4 -oxidation are recorded. $[\alpha]$ are in H_2O . R. S. C.

Conversion of *d*-glucose into *d*-idose. W. H. G. LAKE and S. PEAT (J.C.S., 1939, 1069—1074).—4:6-Dimethyl-2:3-anhydro- β -methylmannoside when heated with NaOMe-MeOH yields 2:4:6-trimethyl- β -methyl-*d*-idopyranoside (I), m.p. 75°, $[\alpha]_D^{18}$ -61.0° in CHCl_3 , converted by aq. H_2SO_4 into 2:4:6-trimethyl-*d*-idose (a syrup), $[\alpha]_D^{18}$ $+26.6^\circ$ in H_2O , $+8.0^\circ$ in CHCl_3 , which with aq. Br gives trimethyl-*d*-idono- δ -lactone, $[\alpha]_D^{17}$ -47.5° in CHCl_3 , -15.4° in H_2O . From this, with liquid NH_3 , 2:4:6-trimethyl-*d*-idonamide, $[\alpha]_D^{17}$ -20.0° in CHCl_3 , is formed. Methylation of (I) ($\text{Ag}_2\text{O-MeI}$) yields tetramethyl- β -methyl- δ -idopyranoside, b.p. 125°/0.02 mm., $[\alpha]_D^{18}$ -68.5° in CHCl_3 , -49.0° in H_2O , -77.3° in MeOH , hydrolysed by aq. H_2SO_4 to tetramethyl-*d*-idopyranose (II) (a syrup), $[\alpha]_D^{18}$ $+14.5^\circ$ in MeOH , $+22.0^\circ$ in H_2O , which on distillation at 130°/0.008 mm. gives octamethyl-*d*-idopyranose, m.p. 102°, $[\alpha]_D^{19}$ $+90.2^\circ$ in CHCl_3 , $+95.0^\circ$ in MeOH , $+103^\circ$ in H_2O , which on hydrolysis with 0.1N- H_2SO_4 regenerates (II). Oxidation of (II) with aq. Br yields tetramethyl-*d*-idono- δ -lactone, m.p. 91°, $[\alpha]_D^{16}$ -52.6° in CHCl_3 , $[\alpha]_D^{13}$ -32.0° in H_2O , which on oxidation with HNO_3 followed by treatment of the

acids with NH_2Me gives *l*-dimethoxysuccinmethylamide and *i*-trimethoxyxyloglutaramethylamide.

J. D. R.

Synthesis of *D*-mannoheptulose; preparation of some of its derivatives. E. D. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1654—1658).—The pulp (21 kg.) of the fruit of *Persea gratissima*, Gaertn., yields *D*-mannoheptulose (I) (315 g.), perseitol (75 g.), a non-reducing gum (400 g.), and a syrup (310 g.) (cf. LaForge, A., 1917, i, 118). In aq. 0.05N- Ba(OH)_2 , *D*-manno-*D*-galactose gives [Lobry de Bruyn rearrangement; $[\alpha] > 68.6^\circ \rightarrow +25.4^\circ$ (in these and other cases $[\alpha]_D^{20}$)] a mixture, which after removal of aldoses by Br-Ba(OBz)_2 affords (I) (25%), m.p. 152°, $[\alpha] +29.2^\circ$ in H_2O , and *D*-glucoheptulose (13%), m.p. 170—174°, $[\alpha] +66.9^\circ$ in H_2O ; in hot $\text{C}_5\text{H}_5\text{N}$ it gives 72% of aldoses with 21% of (I) as sole ketose. With 0.25N- HCl-MeOH , (I) gives α -methyl-*D*-mannoheptuloside (II), m.p. 142°, as sole product since $[\alpha]$ of the final solution ($+71.3^\circ$) is almost that of pure (I) ($+69^\circ$ in H_2O ; this val. decides the configuration). With $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at 0°, (I) gives the α -hexa-acetate, m.p. 100°, $[\alpha] +39.0^\circ$ in CHCl_3 , converted by HBr-AcOH at 0° into the acetobromide, m.p. 92°, $[\alpha] +104.0^\circ$ in CHCl_3 , which with $\text{Ag}_2\text{O-MeOH}$ gives α -methyl-*D*-mannoheptuloside penta-acetate, m.p. 64°, $[\alpha] +49.5^\circ$ in CHCl_3 , obtained also from (II) by $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ at 0° and hydrolysed to (II). Hydrolysis of (II) by 0.005N- HCl at 98° is very rapid (k 0.050), but (II) is nevertheless a pyranoside (a) because it is formed equally, although very rapidly, at 20° and the b.p., and (b) because of its optical relations to *D*-mannose derivatives. R. S. C.

Periodic acid oxidation of $\alpha\alpha$ -trehalose E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1530—1532).—The structure of $\alpha\alpha$ -trehalose is confirmed by oxidation by HIO_4 (4 mols. consumed) to 2 HCO_2H and *D*'*D*'-oxydi-(*D*-hydroxymethylglycollaldehyde), a syrup, converted by Br and SrCO_3 in H_2O into *Sr}_2* *D*'*D*'-oxydi-(*D*-hydroxymethylglycollate) (54%), $+6\text{H}_2\text{O}$, $[\alpha]_D^{20}$ (anhyd.) -24.0° (c 0.29), -52.8° (c 0.91) in H_2O , and the free acid, $[\alpha]_D^{20}$ $+71.3^\circ$ in H_2O , from which by hydrolysis and oxidation (Br) gives $\text{H}_2\text{C}_2\text{O}_4$ and 65% of Ca *D*-glycerate. R. S. C.

Cleavage of cellobiose and celtrobose by emulsin. N. K. RICHTMYER and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 1834—1835).—Cellobiose is hydrolysed 6.8 times as fast as is celtrobose (I) by sweet almond emulsin, the difference being due to the same steric reason as for lactose-neolactose (Helferich *et al.*, A., 1939, II, 99). Hydrolysis of (I) by emulsin, but not by maltase, confirms its β -glucosidic structure. R. S. C.

2:4:6-Trimethyl- β -phenyl- and -benzyl-*D*-glucoside. N. K. RICHTMYER (J. Amer. Chem. Soc., 1939, 61, 1831—1832).— β -Phenyl-*D*-glucoside (isolated or prepared *in situ* from its tetra-acetate) and $\text{Me}_2\text{SO}_4\text{-NaOH}$ at 95° give 2:4:6-trimethyl- β -phenyl-*D*-glucoside, m.p. 108—109°, $[\alpha]_D$ -57.5° in CHCl_3 (with an isomeride, m.p. 105—106°), hydrolysed by hot 5% HCl to 2:4:6-trimethyl-*D*-glucose (I). β -Benzyl-*D*-glucoside gives similarly its 2:4:6-*Me}_3*

derivative, m.p. 94–95°, $[\alpha]_D^{20}$ –49.1° in CHCl_3 , also hydrolysed to (I).
R. S. C.

Flavonol glucoside of *Calystegia japonica*, Chois. G. HUKUTI (J. Pharm. Soc. Japan, 1939, 59, 85–86).—Extraction of the leaves and stems of *C. japonica*, Chois, with MeOH gives *campherol-3-rhamnoglucoside*, $\text{C}_{27}\text{H}_{30}\text{O}_{15} \cdot 2\text{H}_2\text{O}$, m.p. 220–224°, in 0.03% yield. It is hydrolysed by dil. H_2SO_4 to campherol, glucose, and rhamnose and transformed by CH_3N_2 followed by dil. H_2SO_4 into 3-hydroxy-5:7:4'-trimethoxyflavone, m.p. 151°. H. W.

Isolation of monotropitoides from *Gaultheria Cumingiana*, Vidal. M. YASUE and T. SASAKI (J. Pharm. Soc. Japan, 1938, 58, 219).—Extraction of the leaves and twigs of this plant with 50% MeOH, treatment with $\text{Pb}(\text{OAc})_2$, etc. yields *monotropitoides*, $\text{C}_{19}\text{H}_{26}\text{O}_8$, m.p. 181°, $[\alpha]_D^{30}$ –58.8° in H_2O , hydrolysed by 3% H_2SO_4 at 100° to *o*-OH· C_6H_4 · CO_2Me , glucose, and xylose.
R. S. C.

Mol. wt. of beta-amylase from corn starch by means of the ultra-centrifuge. C. O. BECKMANN and Q. LANDIS (J. Amer. Chem. Soc., 1939, 61, 1495–1503).—A modified Beams air-driven ultra-centrifuge has been used to study the sedimentation of β -amylase from maize starch, the granules of which were disrupted by dry grinding for 168 hr. and dispersed in H_2O . The β -amylase thus obtained is of various particle sizes, and mol. wts. range from 17,000 to 225,000. ~50% of the material has a sedimentation const. of 4.0×10^{-13} (mol. wt. 31,000–60,000), whilst the vals. for the whole material range from 1.30 to $>12 \times 10^{-13}$. In the fractionation of ground maize β -amylase by MeOH a light fraction is obtained which is easily pptd. and retrograded. This anomalous behaviour is explained in terms of particle shape and hydration. α -Amylase from maize starch has a sedimentation const. of $\sim 6000 \times 10^{-13}$.
W. R. A.

Mol. wt. of α -amylodextrin (erythro-granulose) from potato starch. C. O. BECKMANN and Q. LANDIS (J. Amer. Chem. Soc., 1939, 61, 1504–1507).—The mol. wts. of α -amylodextrins, prepared by three different methods involving the action of β -amylase on potato starch, vary from 8600 to 29,100. The heterogeneity of the dextrins is discussed. They are more spherical in shape than is β -amylase.
W. R. A.

Constitution of laminarin. Isolation of 2:4:6-trimethylglucopyranose. V. C. BARRY (Sci. Proc. Roy. Dublin Soc., 1939, 22, 59–67; cf. A., 1938, III, 631).—Treatment of the dried comminuted fronds of *Laminaria cloustoni* with aq. $\text{H}_2\text{C}_2\text{O}_4$ (0.25%) for 3 days gives laminarin (I), $[\alpha]_D^{15}$ –12.8° in H_2O . An aq. solution of (I) and dil. HCl slowly deposits an insol. form, the difference in physical properties being thought to be due to the size of the colloidal particles. Acetylation of (I) gives the *triacetate*, $[\alpha]_D^{15}$ –52.0° in CHCl_3 (hydrolysed by 5% MeOH–HCl to α -methylglucoside), methylation of which (Me_2SO_4 + 45% KOH, 7 treatments) gives *trimethyl-laminarin*, $[\alpha]_D^{18}$ –4.39° in CHCl_3 , hydrolysed by 2% MeOH–HCl to 2:4:6-trimethylglucopyranose.

It is suggested that (I) consists of a chain of β -glucopyranose (1:3 linkings) units bent into spiral form.

S. H. H.

tert.-Alkyl primary amines, $\text{CRR}'\text{R}''\text{NH}_2$. I. Ethoxymethyldiallylcarbinylamine and some analogues. B. B. ALLEN and H. R. HENZE (J. Amer. Chem. Soc., 1939, 61, 1790–1794).— $\text{OR} \cdot \text{CH}_2 \cdot \text{CN}$ and $\text{MgR}'\text{Cl}$ give an additive product, which with $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{MgBr}$ (I) yields $\text{OR} \cdot \text{CH}_2 \cdot \text{CR}'(\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2) \cdot \text{NH}_2$. R' may also be allyl. The amines do not give the carbylamine reaction, but their structure is proved by Hofmann degradation of a diallyl compound and synthesis of some of the products. $\text{OR} \cdot \text{CH}_2 \cdot \text{CN}$ ($\text{R} = \text{Me}$, Et , or Pr^i) (1 mol.) and (I) (2 mols.) in Et_2O give ~60% yields of δ -amino- δ -methoxy-, b.p. 187.5–188°/753 mm., δ -ethoxy- (II), b.p. 196–197°/755 mm., and δ -isopropoxy-, b.p. 203–204.5°/753 mm., Δ^4 -heptadiene. Addition of (I) to the product from MgPr^iBr and $\text{OEt} \cdot \text{CH}_2 \cdot \text{CN}$ gives δ -amino- δ -ethoxymethyl- Δ^4 -heptene (III) (60.7%), b.p. 197–198°/753 mm. Hydrogenation (PtO_2 ; AcOH) of (II) or (III) gives δ -amino- δ -ethoxymethyl-*n*-heptane (IV), b.p. 198°/754 mm. (picrate, m.p. 123.5–124.5°). MeI and 40% aq. KOH convert (II) and (IV) into *trimethyl- δ -ethoxymethyl- Δ^4 -heptadien- δ -yl*, m.p. 100.5–101.5° (decomp. at higher temp.), and *trimethyl- δ -ethoxymethyl-*n*-heptyl-ammonium iodide*, decomp. 132.5–133.5°, converted at 150–180°/25–27 mm. into δ -ethoxymethyl- Δ^4 -heptatriene, b.p. 71–72° (uncorr.)/16–17 mm., and Δ^4 -heptene, b.p. 173.5–175°/740 mm., 72–73° (uncorr.)/17 mm., respectively. Hydrogenation (Pt-black ; COMe_3) of both these final products yields δ -ethoxymethyl-*n*-heptane, b.p. 170–171° (uncorr.)/740 mm., also obtained from $\text{CHPr}^i \cdot \text{MgBr}$ and $\text{CH}_2\text{Cl} \cdot \text{OEt}$ in Et_2O . $\text{OEt} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ (prep. from $\text{OEt} \cdot \text{CH}_2 \cdot \text{CN}$ in Pr^iOH by HCl), b.p. 173.5°/748 mm., and MgPr^iBr (2 mols.) give 94.6% of δ -ethoxymethyl-*n*-heptan- δ -ol, b.p. 200–201°/752 mm., which with conc. HCl gives the corresponding *chloride*, b.p. 94–95° (uncorr.)/25 mm.; conversion thereof into (III) could not be achieved. Temp. are corr. n , d , and γ of the products are given, and $[M]$ and the parachors calc.
R. S. C.

Crystal structure of glucosamine [and α -chitosamine].—See A., 1939, I, 457.

Action of periodic acid on α -amino-alcohols. B. H. NICOLET and L. A. SHINN (J. Amer. Chem. Soc., 1939, 61, 1615).— HIO_4 oxidises substances containing *cis*- $\text{CX} \cdot \text{CX}$, in which $\text{X} = \text{OH}$ or NH_2 . Thus, serine gives 95% of CH_2O and (judged by consumption of HIO_4) NH_3 and $\text{CHO} \cdot \text{CO}_2\text{H}$ (slowly further oxidised to CO_2 and HCO_2H). Qual. results with other NH_2 -acids are reported. $\text{NH}[(\text{CH}_2)_2 \cdot \text{OH}]_2$ rapidly gives $4\text{HCO}_2\text{H}$, but $\text{NEt}_2 \cdot (\text{CH}_2)_2 \cdot \text{OH}$ does not react.
R. S. C.

Polyiodides in alcoholic solutions of iodine and hexamethyl- $\alpha\gamma$ -diaminopropan- β -ol iodide. M. COVELLO (Annali Chim. Appl., 1939, 29, 187–189; cf. A., 1937, II, 8).—Ultra-violet absorption spectra indicate the presence of dissociable complexes in 0.05M. and 0.02M. solutions of the propanol with 4, 6, and 8I per mol.
F. O. H.

Guanidomalonic acid.—See A., 1939, III, 707.

Phosphoserine and its enzymic hydrolysis.—See A., 1939, III, 721.

Reaction between organic sulphur compounds and hydrogen peroxide. XVIII. **Action of neutral hydrogen peroxide on thiocarbamides. Synthesis of aminoiminomethanesulphino-betaines.** R. KITAMURA (J. Pharm. Soc. Japan, 1939, 59, 33—36).—Gradual addition of H_2O_2 to $\text{CS}(\text{NH}_2)_2$ in 70% EtOH gives formamidinesulphino-betaine, decomp. 127—128°; *methyl*-, decomp., 95—97°, *propyl*-, decomp. 152—153°, and *diallyl*-, decomp. 89—91°, *-formamidinesulphino*betaine are obtained from the requisite substituted thiocarbamides. All are unstable and are transformed by KOH and H_2O_2 at room temp. into the corresponding carbamides.

H. W.

Action of aldehydes on thiol-amino-compounds. L. GENEVOIS and P. CAYROL (Bull. Soc. chim., 1939, [v], 6, 1223—1230; cf. Schubert, A., 1936, 824).—Neutral solutions of equimols. of cysteine (I) and CH_2O (at p_{H} 4) give the compound, cysteine-formaldehyde (1 to 1 mol.) (stable at p_{H} 4 to p_{H} 7), m.p. $\sim 65^\circ$ (hygroscopic), decomposed by I. MeCHO, EtCHO, and PrCHO act similarly but not completely, and PhCHO much less readily. (I) (1 mol.) reacts with ketones, e.g., COMe_2 , AcCO_2H , or furfuraldehyde, only in large excess, e.g., 20 mols. of COMe_2 ; the equilibrium is discussed. Between p_{H} 3 and 7, (I) acts amphotERICALLY, similarly to other NH_2 -acids. $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{SH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ reacts only with a large excess of CH_2O , e.g., 200 mols. (reaction complete at p_{H} 7.5); MeCHO reacts less readily, and ketones not at all. A definite relationship between NH and SH is essential for positive reaction. Thiolacetic or thiosuccinic acid does not react even with a very large excess of aldehydes or ketones.

A. T. P.

Electrolytic reduction and determination of oxidised glutathione. J. S. DOHAN and G. E. WOODWARD (J. Biol. Chem., 1939, 129, 393—403).—Oxidised glutathione (I) is completely reduced electrolytically in an acid medium using a Hg cathode. The reduced (I) is determined by the sp. glyoxalase method or iodometrically. No oxidised (I) was found in sulphosalicylic acid extracts of blood or tissue but when added it was completely recovered by electrolytic reduction and only partly by reduction with Zn.

E. M. W.

Halogenoacetylcarbamides. I. A. PEARL and W. M. DEHN (J. Amer. Chem. Soc., 1939, 61, 1377—1378).— $\text{CH}_2\text{Cl}\cdot\text{COCl}$ and $\text{CO}(\text{NH}_2)_2$, first at room temp. and then at 100°, give chloroacetylcarbamide, m.p. 190—191° (lit., decomp. 160°, m.p. 180°), sternutatory. *Dichloroacetylcarbamide* (prep. from $\text{CHCl}_2\cdot\text{COCl}$), m.p. 149—150°, is also sternutatory and with NaI in COMe_2 gives *di-iodoacetylcarbamide*, m.p. 192—193°. $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ gives similarly *tri-iodoacetylcarbamide*, m.p. 74—75°, unstable in air. *Dibromoacetylcarbamide*, m.p. 180—181°, is prepared from $\text{CHBr}_2\cdot\text{COBr}$.

R. S. C.

Dimorphism of α -bromoisovalerylcarbamide. A. WATANABE (J. Pharm. Soc. Japan, 1938, 58, 145—149; cf. Ichikawa, A., 1936, 1237).—Cryst. form and

physical consts. are compared for the α - (plates or scales) and β -form (needles or prisms), m.p. 153—154°; the α - at 120—130° gives the β -form.

A. T. P.

Characteristic reaction of dithio-oxamide with ferrous iron. G. NILSSON (Analyst, 1939, 64, 501).—A deep blue colour is produced when excess of cold alkaline aq. dithio-oxamide reacts with a Fe^{II} salt, or with a Fe^{III} salt in presence of a reducing agent. Metallic Fe does not react with the alkaline reagent unless rendered cathodic for a few sec., after which it dissolves with production of a blue colour.

E. C. S.

Hydrolysis of guanidine by boiling potassium hydroxide solution. G. LAUDE (Compt. rend., 1939, 208, 1848—1850; cf. A., 1938, I, 202, and following abstract).—The rate of hydrolysis of equimol. amounts of guanidine, creatine, creatinine, and arginine is the less the greater is the mol. wt.

J. L. D.

Curves showing formation of ammonia by boiling alkaline solutions of guanidine and proteins. G. LAUDE (Compt. rend., 1939, 208, 1691—1692).—Rates of production of NH_3 by alkaline hydrolysis of guanidine, creatine, arginine, and the albumin of egg, blood, and wheat are examined (cf. A., 1937, II, 357; 1938, I, 202).

J. L. D.

Co-ordination by methyl isonitrile. Structure of β -tetramethyl ferrocyanide. H. M. POWELL and G. B. STANGER (J.C.S., 1939, 1105—1106).—The β form of Me_4 ferrocyanide (Hartley, J.C.S., 1913, 103, 1196) is shown by X-ray analysis to be the *trans* six-co-ordinated compound with four MeNC mols. attached to Fe by linkings of the type found in metallic carbonyl compounds.

J. D. R.

Isomerisation of cyclohexane and methylcyclopentane. A. L. GLASEBROOK and W. G. LOVELL (J. Amer. Chem. Soc., 1939, 61, 1717—1720).— AlCl_3 , activated by H_2O or HCl, equilibrates cyclohexane and methylcyclopentane (I) to mixtures containing 12.5% of (I) at 25°, rising to 25.6% at 77.4° (cf. Nenitzescu *et al.*, A., 1933, 941). Thermodynamic consts. are calc.

R. S. C.

Dehydration of *trans*-2-methylcyclohexanol. C. C. PRICE (J. Amer. Chem. Soc., 1939, 61, 1847—1849).—*trans*-2-Methylcyclohexanol and P_2O_5 at any temp. between 140° and 230° give a mixture (A) of 1- (35—50% of the mixture) and 3-methyl- Δ^1 -cyclohexene (structures determined by oxidation), although Vogel's C_7H_{12} and C_7H_{14} (A., 1938, II, 268, 354, 436; 1939, II, 304) resemble 1-ethylcyclopentene and ethylcyclopentane, respectively, in physical properties. (A) is reduced (H_2 , Raney Ni, EtOH), best after distillation with EtOH, to methylcyclohexane (no change in physical properties during 1 month).

R. S. C.

Catalytic cyclisation of paraffin hydrocarbons in presence of platinised charcoal. B. A. KAZANSKI and A. F. PLATE (J. Gen. Chem. Russ., 1939, 9, 496—502).—The following products are obtained by passing the hydrocarbon over Pt-C at 305—310°; from *n*-hexane, C_6H_6 ; from β -methylhexane, PhMe; from γ -methylheptane, PhEt and *o*- and *p*-xylene; from δ -methylheptane, *m*-xylene; from δ -methyl-

octane, PhPr and *m*-C₆H₄MeEt. Diisoamyl passed over Ni-Al₂O₃ catalyst at 350° yields up to 25% of unidentified aromatic products. R. T.

Synthesis and properties of β -phenyloctane, ϵ -phenylnonane, and η -phenyltridecane. A. D. PETROV, A. D. BAIDANOV, N. N. ZAKOTIN, and P. I. SUNTZOV (J. Gen. Chem. Russ., 1939, 9, 509—512).—Mg hexyl bromide and CPhMe yield β -phenyloctan- β -ol, b.p. 136—137°/12 mm., dehydrated by heating in presence of I to β -phenyl- Δ^8 -octene, b.p. 121—122°/10 mm., which with H₂ (Ni catalyst) gives β -phenyloctane, b.p. 125—127°/18 mm., not solidifying at -80°. ϵ -Phenylnonan- ϵ -ol, b.p. 130—132°/7—8 mm., from MgBu⁺Br and EtOBz, similarly yields ϵ -phenyl- Δ^8 -nonene, b.p. 117—121°/6 mm., hydrogenated to ϵ -phenylnonane, b.p. 126—127°/12 mm. η -Phenyltridecan- η -ol, b.p. 165—170°/8 mm., η -phenyl- Δ^8 -tridecene, b.p. 153—154°/8 mm., and η -phenyltridecane, b.p. 183—184°/20° mm., not solidifying at -78°, are obtained analogously. The η of the saturated hydrocarbons varies little with change in temp. R. T.

Rearrangement of 4-tert.-butyl-*m*-xylene with aluminium chloride. L. I. SMITH and H. O. PERRY (J. Amer. Chem. Soc., 1939, 61, 1411—1412).—1:3:4-C₆H₃Me₂Bu⁺, b.p. 113—114°/28 mm., 210—214°/760 mm. [oxidised by KMnO₄ to 1:3:4-C₆H₃(CO₂H)₃], prepared from 1:3:4-C₆H₃Me₂MgI by Bu⁺Cl, is converted by AlCl₃ at 100° into 1:3:5-C₆H₃Me₂Bu⁺ (cf. Baddeley *et al.*, A., 1935, 612) and may thus be an intermediate in the reaction of *m*-xylene and Bu⁺Cl in presence of AlCl₃. R. S. C.

Trinitrotriphenylmethide ion as a secondary and primary base.—See A., 1939, I, 472.

Beryllium chloride in organic reactions. H. BREDERECK, G. LEHMANN, C. SCHÖNFELD, and E. FRITZSCHE (Ber., 1939, 72, [B], 1414—1429).—In its behaviour towards org. chemicals BeCl₂ shows a close analogy to AlCl₃ but usually requires a somewhat higher temp. Reactions which require only a slight activation, *e.g.*, hydrocarbon syntheses with labile halogen compounds, proceed very smoothly whereas difficulty is experienced when stable compounds are involved. The ketone synthesis appears to take place less readily with BeCl₂ than with AlCl₃. It is assumed that the primary substance in the change is an additive compound of the metallic halide and the org. partner which should not be too stable. Such stability is more likely to be met with in the Be derivatives by reason of the smaller ionic radius of the metal and hence more drastic conditions are necessary subsequently. The yields with BeCl₂ and AlCl₃ are somewhat similar but variations occur in both directions and final judgment cannot be pronounced until the optimal conditions for each change have been established. In cases where mol. amounts are required the advantage lies with BeCl₂ by reason of its smaller mol. wt. but economically AlCl₃ remains unchallenged. The following reactions are described in detail: C₆H₆ and CH₂PhCl to CH₂Ph₂ (60%), *o*- and *p*-C₆H₄(CH₂Ph)₂; PhMe and CH₂PhCl to CH₂Ph-C₆H₄Me-*p* and benzyl-*p*-methylbenzylbenzene, b.p. 234—236°/12 mm.; *m*-xylene and CH₂PhCl to

phenylxylylmethane and (phenylxylyl)benzylmethane, b.p. 240—245°/14 mm.; CH₂PhCl and *s*-C₆H₃Me₃ to phenylmesitylmethane, m.p. 36°, and phenyl-2:4:6-trimethylphenylbenzylmethane, b.p. 238—244°/12 mm., m.p. 76°; C₆H₆ and CHPhCl₂ to CHPh₂ (yield 28.5%) and a little CH₂Ph₂; PhMe and CHPhCl₂ to phenyl-*p*-, b.p. 218—220°/12 mm. (yield 73%), and (?) -*o*-, b.p. 286—289°/12 mm., -ditolylmethane; CHPhCl₂ and NPhMe₂ to leucomalachite-green (yield 54.2%); PhMe and EtBr to *p*-C₆H₄MeEt (yield 47%) and C₆H₃MeEt₂, b.p. 195—200°/760 mm.; PhMe and AcCl to *p*-C₆H₄MeAc (yield, 80%); AcCl and C₆H₆ to CPhMe (yield 33%); C₆H₆ and CH₂PhOH to CH₂Ph₂ (yield 58%) and C₆H₄(CH₂Ph)₂, or with less BeCl₂ to CH₂PhCl (yield 57%) which is thus an intermediate in the production of CH₂Ph₂ by this method; CHPh₂OH and BeCl₂ at 100—110° afford CHPh₂Cl in 77% yield; CH₂PhOH and PhMe to CH₂Ph-C₆H₄Me and phenyltolylbenzylmethane; COMe₂ and BeCl₂ at 150° to mesityl oxide (yield 27%) and phorone (yield 12%); COMeEt and BeCl₂ to γ -methyl- Δ^7 -hepten- ϵ -one, b.p. 167—168° (yield 30%); CPhMe to C₆H₃Ph₃ and dypnone; PhCHO and PhMe to phenyl-di-*p*-, b.p. 193°/3 mm., and -*o*- (I), b.p. 270°/3 mm., -tolylmethane [MeOBz and *o*-C₆H₄Me-MgBr give phenyl-di-*o*-tolylcarbinol, m.p. 107—108°, which is reduced to (I), m.p. 104—105°]; CH₂Cl-CO₂Ph and BeCl₂ at 130—140° to *o*- and *p*-OH-C₆H₄-CO-CH₂Cl; *p*-C₆H₄Me-OBz to 2:5:1-OH-C₆H₃Me-COPh, m.p. 84° (yield 69%); *p*-C₆H₄Me-OAc and BeCl₂ to 2:5:1-OH-C₆H₃Me-COMe, converted by HNO₃ (d 1.2) at 100° into 3-nitro-2-hydroxy-5-methylacetophenone, m.p. 132° (Na salt). CPh₂CH₂ is converted by BeCl₂ in C₆H₆ at 110—120° into its dimeride, m.p. 142°, in ~90% yield. C₂H₄ gives the highest yields of distillable polymerisate at 200°/initial pressure 110 atm. At higher temp. carbonisation increases. All fractions are unsaturated; *n*- and *iso*-hexane, hexene, pentanes, pentenes, and butenes have been identified. C₃H₆ at 155—165°/30 atm. gives volatile hydrocarbons (15.3%), benzines (20.7%), light oils (39.3%), and heavy and lubricating oils (24.7 %). All fractions are unsaturated. The gases contain unchanged C₃H₆, butene (II), and isobutene (III). At 200° (III) yields ~80% of benzines consisting mainly of diisobutene and isomeric octenes with some triisobutene and its isomerides. Very little saturated hydrocarbon is present. A tetrameric isobutene, b.p. 101—102°/4 mm., has been identified. The gases contain unchanged (III), C₃H₆, and (II). *iso*Hexene, *iso*pentane, and *isohexane* are present in the volatile distillate. In glass vessels > half of the polymerisate is a yellow, viscous material, not volatile at 360°/vac.; the material of the autoclave appears to have a proper, catalytic influence. *iso*Hexene at ~200°/20—30 atm. gives benzines (54%) consisting of C₈ with some C₁₂ hydrocarbons, *n*- and *iso*-hexane, and *isopentane*. BeO has moderate catalytic activity whereas BeF₂ and Be₂OF₂ have very little effect. BeO appears to accelerate polymerisation rather than cracking, isomerisation, or hydrogenation. Anthracene and phenanthrene are cracked by BeCl₂ to tetrahydronaphthalene, alkyl-benzenes and -naphthalenes, or, under other conditions, to unidentified cryst. compounds. Attempts to crack an aromatic

coal-tar oil were unsatisfactory, only small amounts of benzenoid hydrocarbons being obtained. H. W.

Resonance and physical and chemical properties of diphenyl types. M. CALVIN (J. Org. Chem., 1939, 4, 256—261).—The requirement that the four linkings extending from a double linking >C=C< must be coplanar is applied to the contributing resonating states of diphenyls. Discussion of the effect of non-*o*-substituents on the rate of racemisation of certain diphenyls leads to the prediction that 2 : 2'-di-bromo-4-nitro-4'-aminodiphenyl should be resolvable and have a racemisation half-life >10 min. Consideration of the effect of the possibility or impossibility of conjugated resonating states on the absorption spectrum of substituted diphenyls brings the prediction that certain non-resolvable tetra-*o*-substituted diphenyls should show the conjugated absorption spectrum whereas other tetra-*o*-substituted diphenyls in which the coplanar arrangement of the rings is impossible should have an absorption spectrum very similar to the uncoupled parts. The existence of optically active derivatives of 9 : 9'-diphenanthryl and of 9-cyclohexenylphenanthrene is foretold and the relationship between the contributing resonating states and the reactivity towards a diene condensation is discussed. H. W.

Reaction between hexabromobenzene and magnesium phenyl bromide. T. A. GEISSMAN and R. C. MALLATT (J. Amer. Chem. Soc., 1939, 61, 1788—1790).— C_6Br_6 and MgPhBr give (on hydrolysis) small yields of 1 : 2 : 4 : 5- $\text{C}_6\text{H}_2\text{Br}_4$ and - $\text{C}_6\text{H}_2\text{Ph}_4$ and much tar, the $\text{C}_6\text{H}_2\text{Br}_4$ being formed from $\text{C}_6\text{Br}_4(\text{MgBr})_2$ and the $\text{C}_6\text{H}_2\text{Ph}_4$ from $\text{C}_6\text{Ph}_4(\text{MgBr})_2$, i.e., by independent mechanisms. Carbonation gives 2 : 3 : 5 6-tetraphenylterephthalic acid, m.p. $>320^\circ$ (block) (Me_2 ester, m.p. 280°). C_6Br_6 is unchanged by $\text{Mg} + \text{MgI}_2$, indicating no reaction (above) with Mg or $\text{Mg} + \text{MgBr}_2$. A large excess of MgPhBr doubles the yield of $\text{C}_6\text{H}_2\text{Ph}_4$. C_6Br_6 and LiPh give only polymeric material. C_6Br_6 and MgPhI give 7.9% of $\text{C}_6\text{H}_2\text{Ph}_4$ and much tar.

R. S. C.

Reaction between maleic anhydride and vinylhydrindenes. R. T. ARNOLD (J. Amer. Chem. Soc., 1939, 61, 1405—1406).—Gradual addition of conc. H_2SO_4 to hydrindene, 30% aq. CH_2O , and conc. HCl at 60° gives 5-chloromethylhydrindene (57% yield), b.p. $110\text{—}112^\circ/4$ mm., converted by $(\text{CH}_2)_6\text{N}_4$ in 60% EtOH into hydrindene-5-aldehyde, b.p. $135\text{—}138^\circ/23$ mm., which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and piperidine at 60° yields β -5-hydrindenylacrylic acid (I), m.p. $161\text{—}162^\circ$. α -5-Hydrindenylethyl alcohol [prep. from acetohydrindene (II) by Na-EtOH], b.p. $133^\circ/10$ mm., with HCO_2H or PhNCO gives polymerides, but with $\text{C}_5\text{H}_5\text{N-SOCl}_2$ gives a chloride, converted by KOH-EtOH into 5-vinylhydrindene (III), b.p. $95\text{—}100^\circ/10$ mm., which is obtained also from (I) in 5% yield by thermal decomp. in presence of quinol or Cu-quinoline. MgMeI and (II) give a carbinol, converted by dry HCl at 0° into the chloride, which with KOH-EtOH at 60° yields 5-isopropenylhydrindene, b.p. $84^\circ/2$ mm. This and (III) are polymerised by maleic anhydride in xylene at 100° , showing that either the ethylenic linkings of the

hydrindene ring are not "fixed" by the C:C or that the rate of polymerisation exceeds that of addition.

R. S. C.

Photosensitive nitro-compounds. VI. Certain nitronaphthalene derivatives substituted in the *o*- or *p*-positions with sulphur-containing radicals. N. N. VOROSHOV, V. V. KOZLOV, and I. S. TRAVKIN (J. Gen. Chem. Russ., 1939, 9, 522—525).—1 : 2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ diazotised in aq. H_2SO_4 and then treated with SO_2 (Cu-bronze catalyst) yields 1-nitronaphthalene-2-sulphinic acid, m.p. $119\text{—}5^\circ$. 2 : 1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$ is converted (Sandmeyer with NaNO_2) into 2-nitronaphthalene-1-sulphonic acid.

R. T.

Phenanthrene syntheses with 2 : 3-dimethyl- Δ^2 -cyclohexenone. E. BERGMANN and A. WEIZMANN (J. Org. Chem., 1939, 4, 266—269).—The crude condensation product of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ and $(\text{CH}_2\text{O})_3$ is heated with NaOEt-EtOH at $85\text{—}115^\circ$ and the product is acidified with AcOH , thus giving *Et* 3-methyl- Δ^2 -cyclohexenone-4-carboxylate, b.p. $160\text{—}165^\circ/35$ mm., $108^\circ/1$ mm., which is converted by NaOMe and MeI in MeOH into *Et* 2 : 3-dimethyl- Δ^2 -cyclohexenone-4-carboxylate, b.p. $158\text{—}161^\circ/21$ mm., $104\text{—}110^\circ/1$ mm., transformed by 10% KOH-EtOH into 2 : 3-dimethyl- Δ^2 -cyclohexenone (I), b.p. $53\text{—}65^\circ/1.5$ mm. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$ and (I) afford 3- β -phenylethyl-1 : 2-dimethyl- $\Delta^{1:3}$ -cyclohexadiene, b.p. $155^\circ/6$ mm., converted by SnCl_4 in C_6H_6 saturated with HCl at 0° into 1 : 2-dimethyl-3 : 4 : 9 : 10 : 11 : 12-hexahydrophenanthrene, b.p. $105\text{—}107^\circ/0.02$ mm., $150\text{—}160^\circ/29$ mm., which is dehydrogenated (Se at 330°) to 1 : 2-dimethylphenanthrene, m.p. $142\text{—}143^\circ$, usually accompanied by some 1 : 2-dimethyl-9 : 10-dihydrophenanthrene, b.p. $115\text{—}120^\circ/2$ mm. *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ reacts violently with $(\text{CH}_2)_2\text{O}$, giving *m*-anisylethyl alcohol, b.p. $105\text{—}110^\circ/1$ mm., transformed by SOCl_2 and NPhMe_2 ($\text{C}_5\text{H}_5\text{N}$ gives inconst. results) into *m*-anisylethyl chloride, b.p. $85\text{—}87^\circ/1.5$ mm., $128\text{—}130^\circ/14$ mm., also obtained from *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot(\text{CH}_2)_2\cdot\text{MgCl}$ and (I) yield 3- β -*m*-anisylethyl-1 : 2-dimethyl- $\Delta^{1:3}$ -cyclohexadiene, b.p. $145\text{—}147^\circ/0.8$ mm., cyclised (as above) to 7-methoxy-1 : 2-dimethyl-3 : 4 : 9 : 10 : 11 : 12-hexahydrophenanthrene, b.p. $135^\circ/0.07$ mm. This is dehydrogenated to 7-methoxy-1 : 2-dimethylphenanthrene (*picrate*, m.p. 149°) and 7-methoxy-1 : 2-dimethyl-9 : 10-dihydrophenanthrene, b.p. $\sim 150^\circ/1$ mm.

H. W.

Syntheses in the 1 : 2-benzanthracene and chrysene series. L. F. FIESER and W. S. JOHNSON (J. Amer. Chem. Soc., 1939, 61, 1647—1654).—Some benzantracene and chrysene derivatives are synthesised. Formation of benzantracene or chrysene derivatives by ring-closure sometimes depends on the condensing agent used. When the product obtained from 8-keto-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene (I) and MgEtBr is dehydrated by heating, it gives 88.5% of 8-ethyl-3 : 4 : 5 : 6-tetrahydro-1 : 2-benzanthracene, m.p. $65\text{—}67^\circ$, b.p. $\sim 185^\circ/1$ mm., dehydrogenated by S at $210\text{—}255^\circ$ (followed by Zn dust) to 8-ethyl-1 : 2-benzanthracene, double m.p. $78\text{—}79^\circ$ and $82.5\text{—}83^\circ$ (*picrate*, m.p. $149.5\text{—}150^\circ$). Heating with S at $230\text{—}255^\circ$ (not PtO_2 in C_{10}H_8)

and subsequent distillation converts (I) into 8-hydroxy-1:2-benzanthracene (45%), m.p. 151.3—151.8° (acetate, m.p. 133—133.6°), which with NH_3 and NaHSO_3 in aq. dioxan at 190—200° yields 8-amino-1:2-benzanthracene (26%), m.p. 201.7—202.3° (decomp.). Me γ -keto- γ -9:10-dihydro-2-phenanthrylbutyrate (prep. from the acid by HCl - MeOH), m.p. 77—78°, and MgMeI (slight excess) in boiling Et_2O - C_6H_6 give 53% of γ -9:10-dihydro-2-phenanthryl- Δ^8 -pentoic acid (II) (? mixed stereoisomerides), m.p. 117—125° [a probably pure acid had m.p. 137—138° (decomp.)], but at a lower temp. 32% of (II) is obtained with 35% of γ -9:10-dihydro-2-phenanthryl- γ -valerolactone (III), m.p. 61.5—63° (clear at 70°). (III) is obtained also from (II) by hot 10% H_2SO_4 and with boiling aq. alkali gives the γ -OH-acid, m.p. 95—97° (decomp.). Reduction of (III) by Zn -alkali or Zn - Hg - HCl was unpromising, but H_2 - PtO_2 in AcOH reduces (II) readily to γ -9:10-dihydro-2-phenanthryl-n-valeric acid, m.p. 77.5—78.5°, converted by HF in 81.5% or by PCl_5 in C_6H_6 , followed by AlCl_3 , in 64% yield into 8-keto-5-methyl-3:4:5:6:7:8-hexahydro-1:2-benzanthracene (IV), m.p. 127.9—128.4°. This is converted into 5-methyl-1:2-benzanthracene (49.5% yield) by heating with Zn - Hg in PhMe - AcOH - HCl - H_2O , removing unchanged ketone chromatographically (Al_2O_3), and dehydrogenating with S at 200—255°. Condensation of (IV) with MgMeI (excess) in C_6H_6 and dehydration at 250° gives a mixture, from which 5:8-dimethyl-3:4-dihydro-1:2-benzanthracene, m.p. 82.2—82.8° [absorption spectrum very similar to that of 20-methyl-6:7-dihydrocholanthrene; max. at 2715 ($\log \epsilon$ 4.72) and 3090 Å. ($\log \epsilon$ 4.13)], separates; the residue is converted by S , first at 210—215° and then at 235°, into 5:8-dimethyl-1:2-benzanthracene, m.p. 131.2—131.4° and then 134.4—134.7° (picrate, m.p. 174.5—175°). 8-Methyl-1:2-benzanthracene, POCl_3 , and $\text{NPhMe}\cdot\text{CHO}$ in o - $\text{C}_6\text{H}_4\text{Cl}_2$ at 100° give 8-methyl-1:2-benzanthracene-10-aldehyde (42%), m.p. 151.5—152°, the hydrazone, m.p. 181—181.5° (decomp.), of which with EtOH - NaOEt at 195—208° yields 8:10-dimethyl-1:2-benzanthracene, m.p. 145.5—146.5° (picrate, m.p. 165.5—166°). Me γ -2-phenanthrylbutyrate (prep. from the 9:10- H_2 -ester, b.p. \sim 230°/4—5 mm., by S at 235—255°), b.p. \sim 240°/4 mm., yields the derived acid (V), m.p. 134—135.5°, which with HF gives 78% of 8-keto-5:6:7:8-tetrahydro-1:2-benzanthracene (VI), m.p. 117.5—118.5°; MgMeCl etc. then yields 8-methyl-5:6-dihydro-1:2-benzanthracene, m.p. 80—80.6° [picrate, m.p. 151—152° (decomp.)], and thence (S at 205—245°) 8-methyl-1:2-benzanthracene. However, ZnCl_2 in Ac_2O - AcOH cyclises (V) in 51% yield to 4-keto-1:2:3:4-tetrahydrochrysene (VII); 85% H_2SO_4 at 100° gives 23% of (VII); PCl_5 - C_6H_6 , followed by AlCl_3 , gives 35% of (VI) and 17.5% of (VII), or in PhNO_2 mainly (VI) with very little (VII). MgMeCl , followed by dehydration, converts (VII) into a H_2 -derivative (90%), which with S at 215—245° gives 4-methylchrysene, m.p. 151—151.5° (picrate, red and unstable orange forms, m.p. 137.5—138°). M.p. are corr.

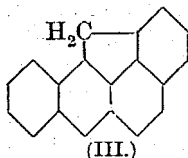
R. S. C.

Photo-oxides of carcinogenic hydrocarbons.
J. W. COOK, R. MARTIN, and E. M. F. ROE (Nature, C C (A., II)

1939, 143, 1020).—Passage of O_2 through a 0.05% solution of 9:10-dimethyl-1:2-benzanthracene in CS_2 exposed to the light of a 200-w. gas-filled lamp gives a photo-oxide (I), m.p. 193—194°. Photo-oxides (m.p. in parentheses) have been obtained equally readily from 5:9:10- (212—213°) and 6:9:10-trimethyl- (II) (205—206°), 5:6:9:10-tetramethyl-1:2-benzanthracene (III) (228—229°), and 9:10-dimethyl-1:2:5:6-dibenzanthracene (222—223°). (II) has m.p. 157—158°, and (III), m.p. 132—133°. The ultra-violet absorption spectrum of (I) shows bands similar to those of a meso- H_2 -derivative of 1:2:5:6-dibenzanthracene, with \sim half their intensities. Irradiation (Hg arc) of a C_6H_{14} solution of (I) causes decomp. and the spectrum of the parent hydrocarbon reappears. The spectrum of 9:10-dihydroxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene shows bands of the same order of intensity as the photo-oxide, but shifted \sim 180 Å. towards the far ultra-violet. 1:2-Benzanthracene, but not 1:2:5:6-dibenzanthracene and 3:4-benzpyrene, gives indications of the formation of a photo-oxide.
L. S. T.

Synthesis of 1':9-methylene-1:2-benzanthracene and related hydrocarbons.

L. F. FIESER and J. CASON (J. Amer. Chem. Soc., 1939, 61, 1740—1745).—Acenaphthene and AcOH or AcCl in HF give 1- (I) (29%), m.p. 114—114.5° [picrate, m.p. 114.5—115°; $\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 113.5—114°], and 3-acetoacenaphthene, m.p. 69—69.5° (picrate, orange and yellow forms, m.p. 97—97.5°), both stable in HF . KOCl in aq. dioxan at 60° oxidises (I) to 1-acenaphthoic acid (95.5%), m.p. 254—256°, which with $\text{Na}_2\text{Cr}_2\text{O}_7$ - AcOH at 90—95° give 2-carboxy-1:8-naphthalic anhydride, m.p. 297.5—298.5° (Me ester, m.p. 191—192°), and with SOCl_2 gives 1-acenaphthoyl chloride, m.p. 110—111° (with AlCl_3 in C_6H_6 gives a substance, decomp. $>200^\circ$), and thence by NH_3 in aq. dioxan the amide, m.p. 227—228°. With MgPhBr this gives 1-benzoylacenaphthene (II), m.p. 91.5—92°, b.p. 210—215°/1 mm., obtained also from Mg 1-acenaphthyl iodide and PhCN . Pyrolysis of (II) at 425° gives 1':9-methylene-1:2-benzanthracene (III) (13%), m.p. 122.7—123.1° [picrate, m.p. 141.5—142°; $\text{C}_6\text{H}_3(\text{NO}_2)_3$ derivative, m.p. 162.5—163°]. 1:2:3- $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NO}_2$ and H_2 - PtO_2 in AcOH give 1:2:3- $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NH}_2$, m.p. 40—40.6° (lit., 41—42°); for prep. of 1:3:2- $\text{C}_6\text{H}_3\text{MeClI}$ (IV), m.p. 27.3—27.6° (lit., -26°), b.p. 123—123.5°/14 mm., by the diazo-reaction from 1:2:3- $\text{C}_6\text{H}_3\text{MeI}\cdot\text{NH}_2$ it is best (74.5% yield) to omit isolation of the amine. Grignard reactions of (IV) with CO_2 , 2- $\text{C}_{10}\text{H}_7\cdot\text{COMe}$, or 2- $\text{C}_{10}\text{H}_7\cdot\text{CN}$ give poor yields of indefinite materials, probably owing to steric hindrance of the I. 1:2:3- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2$ (prep. in 92% yield from the NO_2 -compound by Fe - H_2O or H_2 -catalyst), b.p. 98—100°/11 mm., gives (diazo-reaction) 40% of 1:2:3- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CN}$, b.p. 105—107°/11 mm., which with 1- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$ in Et_2O - C_6H_6 and later in hot C_6H_6 yields 89% of 3-o-xylyl α - C_{10}H_7 ketone, b.p. 190—195°/1 mm. Pyrolysis thereof with a little Zn dust



at 425—430° yields 5- and 8-methyl-1:2-benzanthracene (V) and 1:2-benzanthracene. 3-o-Xylyl β -C₁₀H₇ ketone (similarly prepared), m.p. 62—63°, gives a mixture, from which (V) is separable with difficulty. 2-Aceto-1:8-naphthalic anhydride, m.p. 219—219.3°, is obtained by oxidation (Na₂Cr₂O₇-AcOH) of (I). M.p. are corr. R. S. C.

New syntheses of the red hydrocarbon rubicene. V. I. CHMELEVSKI and I. J. POSTOVSKI (J. Gen. Chem. Russ., 1939, 9, 620—624).—Mg and boiling fluorenone give rubicene, in 11% yield. 9:10-Dihydroxy-9:10-diphenyl-9:10-dihydroanthracene with AlCl₃ and MnO₂ (30 min. at 100°) affords rubicene in 4% yield. R. T.

Naphthylaminoalkanes. F. F. BLICKE and C. E. MAXWELL (J. Amer. Chem. Soc., 1939, 61, 1780—1782).—C₁₀H₈ derivatives of benzedrine and similar types have only slight pressor activity (dogs) and produce tolerance and cross-tolerance for ephedrine. When 1-C₁₀H₇·CH₂Cl and (CH₂)₆N₄ are heated in CHCl₃ and the product is distilled with conc. HCl and EtOH, there is obtained 1-C₁₀H₇·CH₂·NH₂, b.p. 200—205°/30 mm. (hydrochloride, new m.p. 260—262°). 1-C₁₀H₇·MgBr with MeCN in Et₂O, followed by aq. HCl, gives 1-C₁₀H₇·COMe, b.p. 145—147°/6 mm., the oxime, new m.p. 134—135°, of which with Na-EtOH yields 1-C₁₀H₇·CHMe·NH₂, b.p. 141—142°/5 mm. [hydrochloride, m.p. 236—237° [lit., 220—221° (decomp.)]]. 2-C₁₀H₇·CMe·N·OH, m.p. 142—143°, yields similarly 2-C₁₀H₇·CHMe·NH₂, b.p. 172—174°/29 mm. [hydrochloride, m.p. 279—280° (lit., 199—200°)]. 1-C₁₀H₇·COEt (prep. from 1-C₁₀H₇·MgBr and EtCN), b.p. 171—172°/12 mm., gives the oxime, new m.p. 55—57°, and thence 1- α -amino-*n*-propylnaphthalene, b.p. 148—149°/10 mm. (hydrochloride, m.p. 281—282°). 1-C₁₀H₇·CH₂Cl and CHNa(CO₂Et)₂ in C₆H₆ give 1-C₁₀H₇·CH₂·CH(CO₂Et)₂, b.p. 199—201°/3 mm., converted by MeI and Na-EtOH into Et₂ α -naphthylmethylmethylmalonate (I), m.p. 51—52°, b.p. 207—209°/2 mm., which with KOH in 60% KOH gives the malonic acid, m.p. 172—173° (decomp.); heating at 175—180° then yields β -1-naphthylisobutyric acid (II), m.p. 91—92°, the amide, m.p. 134—135°, of which with NaOBr at 70—80° gives 1- β -amino-*n*-propylnaphthalene (hydrochloride, m.p. 213—214°). Crude, oily 1-C₁₀H₇·CH·CMe·COMe, obtained from 1-C₁₀H₇·CHO, COMeEt, and HCl, is oxidised by NaOBr to 1-C₁₀H₇·CH·CMe·CO₂H, m.p. 149—150°, which is reduced to (II) by 4% Na-Hg in aq. Na₂CO₃. 1-C₁₀H₇·COPr^a (prep. from 1-C₁₀H₇·MgBr and Pr^aCN), b.p. 155—157°/3 mm., gives the oxime, b.p. 185—187°/8 mm., and thence 1- α -amino-*n*-butylnaphthalene, b.p. 142—143°/4 mm. (hydrochloride, m.p. 281—282°). (I) affords 5- α -naphthylmethyl-5-methylbarbituric acid, m.p. 127—128°. R. S. C.

Thio-acyl derivatives of primary amines (synthesis of acyclic carbocyanine dyes). I. L. KNUNIANZ and L. V. RAZVADOVSKAJA (J. Gen. Chem. Russ., 1939, 9, 557—570).—CH₂Ph·NH·CSMe and MeI at 0° yield the hydriodide, m.p. 104—106° (decomp. by aq. K₂CO₃), of thioacetbenzylamide S-Me ether, SMe·CMe·N·CH₂Ph, b.p. 115—118°/4 mm.,

the methiodide, m.p. 120°, of which is condensed with CH(OEt)₃ or the anililide of CO₂H·CH₂·CHO or of glutacetaldehyde in boiling Ac₂O to the dyes, CHR:CHR', R·[CH:CH]₂·R', or R·[CH:CH]₃·R' [R = CH₂Ph·NMe·C(SMe):CH·, and with *p*-NMe₂·C₆H₄·CHO to give the dye, CH₂Ph·NMe·C(SMe):CH:CH·C₆H₄·NMe₂·*p*. NHMeAc and P₂S₅ in C₆H₆ (70 min. at the b.p.) followed by MeI yield thioacetmethylamide S-Me ether, b.p. 132—133°, the methiodide of which is condensed as above, to yield the corresponding dyes [R = NMe₂·C(SMe):, R' = NMe₂·C(SMe):CH·]. The absorption spectra (in EtOH) of the dyes are given. The sensitising action of the dyes on photographic emulsions is similar to that of the corresponding thiazoline dyes. R. T.

Quenching of fluorescence and photothermal decomposition of aniline.—See A., 1939, I, 404.

Diazotisation and nitrosation of amines. IV. General interpretation of the reaction. J. C. EARL and N. G. HILLS (J.C.S., 1939, 1089—1092; cf. A., 1939, II, 207).—Decomp. of 0.15*N*-aq. NHMe₂·HNO₂ at 5° is accelerated by HCl or H₂SO₄, the rate being a max. with 0.5 mol. of acid. The conductivity during nitrosation of 0.01*M*-aq. NHPhMe at 5° falls with time; if HCl is present, an initial fall is followed by a rise, the amount of which increases with the amount of HCl (0.1—0.3 mol.). NHPhMe·HNO₂ disappears from H₂O in presence of acids at a regular rate, increased by increasing the concn. of acid. These and previous results are explained as due to a primary reaction, OH·N·O + NHR₂ \rightarrow (OH)₂N·NR₂. The reported third-order rate for similar reactions is reconciled with this reaction by considering the effects of ionic dissociation on the various systems involved. R. S. C.

Separated auxo-enoid systems. VI. Coloration of nitrobenzyl derivatives of aromatic amines. V. A. ISMAILSKI and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1939, 9, 647—662).—The coloration of nitrobenzyl derivatives of aromatic amines is ascribed to interaction between the NO₂·C₆H₄·CH₂· and ·NHPh groups. Similar relations between structure and intensity of coloration are found as for the analogous nitro-azo-compounds. R. T.

Preparation of nuclear-substituted dimethylanilines. D. P. EVANS and R. WILLIAMS (J.C.S., 1939, 1199—1200).—Alternate addition, in portions, of Me₂SO₄ (in total a slight excess) and 30% NaOH (to keep the solution alkaline to phenolphthalein) to nuclear-substituted anilines gives the dimethylaniline or its methosulphate in 40—94% yield; the *tert.* amine is readily obtained from the methosulphate by treating the derived methiodide with NaOH in boiling C₂H₅·OH or, less well, by treating with Ag₂O and heating the methohydroxide. *o*-OPh·C₆H₄·NH₂ gives *o*-phenoxydimethylaniline, m.p. 34.5°, b.p. 161—162°/13 mm., and *o*-OPh·C₆H₄·NMe₂·OH. 2-Dimethylaminodiphenyl, b.p. 145.5°/11 mm., and *p*-phenoxydimethylaniline, b.p. 185°/13 mm., m.p. 34°, are described. R. S. C.

Substituted acetylenes and their derivatives.

XXXIV. Addition of arylamines to alkynes. J. A. LORITSCH and R. R. VOGT (J. Amer. Chem. Soc., 1939, 61, 1462—1463; cf. A., 1939, II, 400).— NH_2Ph adds to $n\text{-C}_5\text{H}_{11}\cdot\text{C}\equiv\text{CH}$ (I) or Δ^7 -octinene in presence of HgO and $\text{Et}_2\text{O}\cdot\text{BF}_3$ to give *N*- α -methyl-*n*-hexylideneaniline, b.p. 88—90°/4 mm., and the anil, $\text{CPrBu}\cdot\text{NPh}$, b.p. 95—97°/4 mm., respectively. A *by-product*, $\text{C}_{20}\text{H}_{33}\text{N}$, b.p. 138—141°/4 mm., is obtained in the former reaction. The structure of the anils is proved by acid hydrolysis to NH_2Ph and the ketone. NHPPhEt and (I) give *N*-ethyl-*N*- α -methylene-*n*-hexylaniline, b.p. 92—94°/4 mm. (hydrolysed to $\text{COMe}\cdot\text{C}_6\text{H}_{11}$ and NHPPhEt), and a *by-product*, $\text{C}_{22}\text{H}_{37}\text{N}$, b.p. 146—149°/4 mm. NPhEt_2 does not add to (I). R. S. C.

Naphthalene series. VIII. Preparation of 4-nitro-1-naphthylamine and of an azo-dye derived therefrom. N. N. VOROSHOV and V. V. KOZLOV (J. Gen. Chem. Russ., 1939, 9, 587—589).—1:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NO}$ is oxidised (KMnO_4) to 1:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NO}_2$, m.p. 196°, the diazo-derivative of which when coupled with $m\text{-C}_6\text{H}_4(\text{OH})_2$ yields a bluish-red azo-dye. R. T.

Phenyl- and naphthyl-urethanes and the corresponding disubstituted carbamides. P. JANNKE (J. Amer. Pharm. Assoc., 1939, 28, 360—364).—Formation of $\text{CO}(\text{NHAr})_2$ (I) during prep. of phenyl- and naphthyl-urethanes is discussed with reference to the work of Sherk (A., 1921, i, 239, 240). Solubility data (EtOH and $\text{C}_2\text{H}_4\text{Cl}_2$) for the urethanes of thymol, carvacrol, and thymoquinol and for $\text{CO}(\text{NHPh})_2$ and $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_7\cdot\alpha)_2$ indicate that $\text{C}_2\text{H}_4\text{Cl}_2$ is a suitable solvent for separating the urethane and corresponding (I). F. O. H.

Derivatives of sulphanilamide.—See B., 1939, 884, 885.

Nitration of 3:3'-dichloroazoxybenzene and reduction of some of the products. H. E. BIGELOW and W. H. STEEVES (Canad. J. Res., 1939, 17, B, 160—165).—Reduction of $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ with Na_3AsO_3 in NaOH yields 3:3'-dichloroazoxybenzene (I), which with boiling HNO_3 (d 1.45) gives a mixture of 3:3'-dichloro-6-nitro- (II), m.p. 116°, -4-nitro- (III), m.p. 145°, -2-nitro-, m.p. 112°, -5-nitro-, m.p. 105°, and -4:6-dinitro-azoxybenzene, m.p. 157°. Reduction of (II) with $\text{Sn}\text{-HCl}$ gives $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ (IV) and 4:1:2- $\text{C}_6\text{H}_3\text{Cl}(\text{NH}_2)_2$; similarly (III) gives (IV) and 2:1:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NH}_2)_2$. With fuming HNO_3 , (I) gives 3:3'-dichloro-2:4:6-trinitroazoxybenzene, m.p. 165° [also formed from (II) or (III) with fuming HNO_3], and an isomeride, m.p. 182°. Reduction of (III) with Na_3AsO_3 yields the corresponding tetrachloroazobisazoxybenzene, m.p. 210°, and a small quantity of tetrachlorotrisazoxybenzene, m.p. 195°. Reduction of (II) gave a Cl-free substance, exploding at 275° (hydrochloride, m.p. 178°). J. D. R.

Structure and absorption spectra of azo-dyes. W. R. BRODE (Proc. Sixth Conf. Spectros., 1938, 128—133).—The absorption spectra of a series of halogen-substituted benzeneazophenols have been investigated. It has been found that an increase in mol. wt. is usually accompanied by a decrease in

frequency of the absorption bands which is approx. \propto increase in mol. wt., but varies with position of substitution. Substitution in the p' -position by NO_2 , Me, or halogen causes a max. in the magnitude of the absorption bands in all solvents. Halogen substitution in the oo' -positions causes a very marked decrease in the magnitude of the absorption bands in all solvents. In op' -disubstituted compounds, the p' -substituent exerts a greater effect on the frequency of the absorption max. in EtOH , the o -substituent having more effect on the extinction of the band. Br has a greater extinction effect than Cl. The principal absorption bands of the compounds in NaOH consist of two overlapping bands which may be due to two forms of vibration of the mol. in equilibrium. Cl-derivatives appear to exist in four equilibrium levels and Br-derivatives in six. An investigation of the formation of the chelate ring between o -hydroxyazo-dyes and metallic salts has been carried out by studying the absorption spectra of the complexes and of a series of related compounds possessing certain structural units in common with the complexes. The Cu complex of 3-benzeneazo- p -

cresol exists in azoid, $\text{C}_6\text{H}_3\text{Me}\begin{matrix} \nearrow \text{N}\cdot\text{NPh} \\ \searrow \text{O}\cdot\text{M} \end{matrix}$, and quinoid,

$\text{C}_6\text{H}_3\text{Me}\begin{matrix} \nearrow \text{N}\text{-NPh} \\ \searrow \text{O}\rightarrow\text{M} \end{matrix}$, forms in equilibrium. The structures of $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I) and of the Schiff's bases formed from PhCHO and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and from (I) and NH_2Ph have been investigated.

A. J. M.

Action of mixed organo-magnesium compounds on benzaldehydeacylphenylhydrazones. Preparation of α -acyl- β -alkylphenylhydrazines. P. GRAMMATICAKIS (Compt. rend., 1939, 208, 1910—1912; cf. A., 1937, II, 287).— $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{AcPh}$ (I) with MgEtBr gives *N*-acetyl-*N*-phenyl-*N'*- α -phenyl-propylhydrazine, b.p. 182—184°/1 mm. (phenyl-carbamyl derivative, m.p. 153°), and a little $\text{CHPh}\cdot\text{N}\cdot\text{NHPH}$ (II). (I) or benzaldehydecarbamyl-phenylhydrazone (III) with MgMeI gives (II) almost entirely. (I) or (III) with MgPhBr gives mainly (II) as well as products of interaction of (II) with MgPhBr [β -benzylhydriylphenylhydrazine, m.p. 77°, $\text{CPh}_2\cdot\text{N}\cdot\text{NHPH}$, $\text{CPh}_2\cdot\text{NH}$, NH_2Ph , $\text{CPh}_2\cdot\text{NPh}$, and small amounts of $(\text{CHPh})_2$]. $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{BzPh}$ (IV) with MgPhBr gives *N*-benzoyl-*N*-phenyl-*N'*-benzylhydriyl-hydrazine, m.p. 145°, as well as $\text{CPh}_2\cdot\text{NH}$, $\text{NHPH}\cdot\text{Bz}$, $\text{CPh}_2\cdot\text{OH}$, and (II). (IV) with MgMeI or MgEtI gives mainly *N*-benzoyl-*N*-phenyl-*N'*- α -phenylethyl-, b.p. 195°/1 mm., or -*N'*- α -phenylpropyl-hydrazine, b.p. 198°/1 mm., as well as small amounts of (II), $\text{CPhAlk}\cdot\text{NH}$, and $\text{NHPH}\cdot\text{Bz}$. Benzaldehydphenyl-carbamylphenylhydrazone (V) with MgMeI , MgEtBr , and MgPhBr gives, respectively, *N*-phenylcarbamyl-*N*-phenyl-*N'*- α -phenylethyl-, m.p. 144°, -*N'*- α -phenyl-propyl-, m.p. 102°, and -*N'*-benzylhydriyl-hydrazine, m.p. 214°. In each case 1:3:4-triphenyl-1:2:4-triazol-5-one, m.p. 224°, is formed by intramol. oxidation of (V).

J. L. D.

Germicidal action and chemical constitution of isomeric xylenols and monohalogenated derivatives. K. HEICKEN (Angew. Chem., 1939,

sponding alcohol (II), m.p. 120—121°, which is oxidised (CrO_3 in AcOH) to the aldehyde (III), m.p. 83·5—84·5°; (I) and $(\text{CH}_2)_6\text{N}_4$ in boiling aq. EtOH give impure (II). AlCl_3 in boiling light petroleum demethylates (III) to 6-hydroxy-3-methoxy-2:4:5-trimethylbenzaldehyde, m.p. 88—89°, with probably 3:6-dihydroxy-2:4:5-trimethylbenzaldehyde, possibly two modifications, yellow, m.p. 129—131°, and orange, m.p. 147—148°, obtained in poor yield from trimethylquinol (IV), $\text{Zn}(\text{CN})_2$, and HCl in Et_2O . 3:6-Diethoxy- ψ -cumene, b.p. 102—103°/2 mm., m.p. 34—35°, obtained from the quinol, Et_2SO_4 , and KOH in boiling MeOH , is converted successively into 3:6-diethoxy-2:4:5-trimethylbenzyl chloride, m.p. 86—87°, the acetate, m.p. 113·5—114·5°, and the alcohol, m.p. 112—113°, which is oxidised to the phototropic 3:6-dihydroxy-2:4:5-trimethylbenzaldehyde, m.p. 99—100°. Dealkylation occurs even less readily than with the corresponding $(\text{OMe})_2$ -compounds. (IV) and CH_2PhCl in presence of alkali or $\text{C}_5\text{H}_5\text{N}$ give a difficultly separable mixture (mainly of $\text{C}-\text{CH}_2\text{Ph}$ compound and unchanged material) also obtained from the MgBr salt in Et_2O . 3:6-Dibenzoyloxy- ψ -cumene, m.p. 72·5—73·5°, is obtained in small yield from the quinol and CH_2PhCl in boiling COMe_2 containing K_2CO_3 . (IV) is converted by the successive action of NaOEt and $\text{CH}_2\text{Br}-\text{CO}_2\text{Me}$ followed by hydrolysis into 3:6-dicarboxymethoxy- ψ -cumene, m.p. 205—206°, which appears to be unaffected by successive treatments with SOCl_2 and AlCl_3 in C_6H_6 but is transformed by warm 95% H_2SO_4 into 4-carboxymethoxy-3:5:6-trimethylcoumaranone, m.p. 211—213°. Similarly 3:6-di- α -carboxyethoxy- ψ -cumene is obtained as an oil. ψ -Cuminoquinol diacetate (pure), 40% CH_2O , and HCl are maintained at 10—20° while a fairly rapid stream of HCl is passed, after which the mixture is warmed to 25° and saturation is continued, thus giving 3:6-diacetoxy-2:4:5-trimethylbenzyl chloride, m.p. 150—151°, often accompanied by a by-product, m.p. 225—227°. With $\text{CHAcNa}-\text{CO}_2\text{Et}$ in C_6H_6 it affords *Et* 3:6-dihydroxy-2:4:5-trimethylbenzylacetate, m.p. 135—136° (decomp.). H. W.

Pyrogallol-acetone condensation products. A. VON WACEK and K. KRATZL (Österr. Chem.-Ztg., 1939, 42, 286—289).—No CMe_2 derivative could be obtained directly from pyrogallol, but the appropriate 1-derivatives with COMe_2 and P_2O_5 in COMe_2 give 2:3-isopropylidenepyrogallol 1-Me ether, b.p. 113—115°/17 mm. (hydrolysed by 20% H_2SO_4 to pyrogallol 1-Me ether), 1-benzoate, m.p. 78°, and 1-benzenesulphonate, m.p. 84°. Pyrogallol 1-acetate gives an impure 2:3- CMe_2 derivative (I), b.p. 123—128°/12 mm., hydrolysed by 5% KOH at room temp. to 1:2-isopropylidenepyrogallol (II), m.p. 89—90° (no FeCl_3 reaction), whence (I) is obtained pure (m.p. 47—48°) by hot Ac_2O . The homologue, 1:2:3- $\text{OMe}-\text{C}_6\text{H}_3:\text{O}_2\text{CMeEt}$, b.p. 129—132°/12 mm., is similarly obtained. (II) is termed *gallacetoin*, and its derivatives are named accordingly. R. S. C.

Synthesis of diphenyl ethers containing methoxy- and ethoxy-groups. H. KING (J.C.S., 1939, 1165—1168).— $o\text{-OEt}-\text{C}_6\text{H}_4\text{-OH}$ (1·5), $o\text{-C}_6\text{H}_4\text{-Br}-\text{OEt}$ (1), KOH (1·5 mols.), and a little Cu -bronze at 190—

200° give *di-o-phenetyl ether*, m.p. 53°, b.p. 140—145°/0·5 mm. *o-Anisyl o-phenetyl ether*, m.p. 91—92°, b.p. 150°/0·6 mm., is similarly prepared. 4:3:1- $\text{OH}-\text{C}_6\text{H}_3(\text{OMe})-\text{CO}_2\text{H}$ (Ac derivative, m.p. 144°) is obtained in nearly 86% yield from 4:3:1- $\text{OAc}-\text{C}_6\text{H}_3(\text{OMe})-\text{CHO}$ by $\text{KMnO}_4-\text{COMe}_2$, followed by 2N- NaOH at room temp. 4:5:3:1- $\text{OH}-\text{C}_6\text{H}_2\text{Br}(\text{OMe})-\text{CO}_2\text{H}$, m.p. 231° (lit. 221°), and Et_2SO_4 in 2N- NaOH at 90° give 5-bromo-3-methoxy-4-ethoxybenzoic acid, m.p. 141—142°, and its *Et* ester (I), m.p. 25—26°, b.p. 197°/15 mm. With KOPh (1·5 mols.) and a little Cu powder at 180—190°, followed by $\text{MeOH}-\text{KOH}$, (I) gives 5-carboxy-3-methoxy-2-ethoxydiphenyl ether (II), m.p. 116—117°, and, by debromination, 4:3:1- $\text{OEt}-\text{C}_6\text{H}_3(\text{OMe})-\text{CO}_2\text{H}$. 4-Acetoxy-3-ethoxybenzaldehyde (prep. from the OH -aldehyde by Ac_2O and N- KOH), m.p. 48—49°, with KMnO_4 in COMe_2 gives 4-acetoxy-, m.p. 152—153°, hydrolysed to 4-hydroxy-3-ethoxybenzoic acid, m.p. 164—165°. $\text{Br}-\text{AcOH}$ then gives 5-bromo-4-hydroxy-3-ethoxybenzoic acid (III), +3 or 2 H_2O , m.p. 207°, and 2:4-dibromo-6-ethoxyphenol, m.p. 110°. $\text{Me}_2\text{SO}_4-2\text{N}-\text{NaOH}$ converts (III) into *Me* 5-bromo-4-methoxy-3-ethoxybenzoate (IV), m.p. 77—78°, less of the corresponding acid, m.p. 183—184°, and a small amount of *Me* 5-bromo-4-hydroxy-3-ethoxybenzoate, m.p. 111—112°. With KOPh (1·5 mols.) and Cu powder at 180°, (IV) gives 5-carboxy-2-methoxy-3-ethoxydiphenyl ether (V), double m.p. 117—118° and 134° (sometimes 134° only), and 4-methoxy-3-ethoxybenzoic acid, m.p. 165°. With Cu powder in boiling quinoline, (II) and (V) give CO_2 and 3-methoxy-2-ethoxy-, m.p. 33—34°, b.p. 155°/2 mm., and 2-methoxy-3-ethoxy-diphenyl ether, m.p. 23°, b.p. 138—141°/0·5 mm., respectively. R. S. C.

Constitution of rhapontin. S. KAWAMURA (J. Pharm. Soc. Japan, 1938, 58, 83—85).—Rhapontin from Turkey rhubarb root is a glucoside of *rhapontigenin*, identified as 3:5:3'-trihydroxy-4'-methoxystilbene (I), m.p. 190—191°, the tribenzoate, m.p. 142°, of which is oxidised by CrO_3-AcOH to benzoyl isovanillic (II) and dibenzoylresorcylic acids. With O_3 in AcOH , (I) gives *isovauillin* and α -resorcinolaldehyde. With $\text{Pt}-\text{H}_2$ it gives *dihydorrhapontigenin* (3:5:3'-trihydroxy-4'-methoxydibenzyl), m.p. 135—136° (tribenzoate, m.p. 106—107°). With Ac_2O and with $\text{NaOAc}-\text{Ac}_2\text{O}$, (I) gives *triacetates*, m.p. 114° and 128°, regarded as *cis-trans* isomerides. Since rhapontin benzoate with CrO_3 gives (II) and a Na_2CO_3 -insol. substance, the glucose mol. is presumably attached to a resorcinol-O atom. E. W. W.

Preparation and behaviour of mixed diacyl derivatives of *o*-aminophenol containing a carboxyloxy radical and the *p*-toluenesulphonyl group. L. C. RAIFORD and J. R. SHELTON (J. Org. Chem., 1939, 4, 207—219).— $o\text{-NH}_2-\text{C}_6\text{H}_4\text{-OH}$ and 3:5:1:4- $\text{NH}_2-\text{C}_6\text{H}_2\text{BrMe}-\text{OH}$ (I) have been converted into mixed diacyl derivatives in which one of the radicals was invariably $p\text{-C}_6\text{H}_4\text{Me}-\text{SO}_2$. When the other radical was CR_2O , $\text{OR}-\text{C}=\text{O}$ or $\text{Ar}-\text{C}=\text{O}$ isomerides were obtained when the acyls were introduced in different orders and no migration was observed. When the second radical was $\text{OAr}-\text{C}=\text{O}$ isomeric mixed compounds were again formed but

under these conditions the products may suffer further change. Thus, the *N*-*p*-toluenesulphonyl derivative of each base reacts with ClCO_2Ph to give the expected $\text{O}\cdot\text{CO}_2\text{Ph}$ derivative. That formed from the first base loses PhOH immediately to give the corresponding *N*-*p*-toluenesulphonylbenzoxazolone; with the second base both diacyl derivatives and the substituted benzoxazolone are obtained. Acylations are effected by the method of Einhorn and Hollandt or by that of Groenvik. Where these methods are unsatisfactory good results are obtained by treatment of the aminophenol with NPhMe_2 and the acid chloride in dioxan. The following derivatives of $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ appear new: *N*-benzoyl-*O*-*p*-toluenesulphonyl-, m.p. 109—110°; *O*-benzoyl-*N*-*p*-toluenesulphonyl-, m.p. 141°; *N*-carbethoxy-*O*-*p*-toluenesulphonyl-, m.p. 72—74°; *O*-carbethoxy-*N*-*p*-toluenesulphonyl-, m.p. 128—130°. (I) gives the following derivatives: *N*-*p*-toluenesulphonyl- (II), m.p. 171—172°; *N*-acetyl-*O*-*p*-toluenesulphonyl-, m.p. 131—132°; *O*-acetyl-*N*-*p*-toluenesulphonyl-, m.p. 150—151.5°; *N*-benzoyl-*O*-*p*-toluenesulphonyl-, m.p. 149—151°; *O*-benzoyl-*N*-*p*-toluenesulphonyl-, m.p. 163—164°; *N*-carbethoxy-*O*-*p*-toluenesulphonyl-, m.p. 124.5—125°, hydrolysed to 5-bromo-6-hydroxy-3-methylphenylurethane, m.p. 83°; *O*-carbethoxy-*N*-*p*-toluenesulphonyl-, m.p. 140—142°. *o*-Aminophenyl *p*-toluenesulphonate and ClCO_2Ph afford *o*-carbophenoxyaminophenyl *p*-toluenesulphonate, m.p. 114°, which gives only a dark oil when hydrolysed with $\text{KOH}\cdot\text{EtOH}$. 2-*p*-Toluenesulphonamidophenol and ClCO_2Ph in $\text{C}_5\text{H}_5\text{N}$ or according to Schotten-Baumann yield unchanged material and a little 2-*p*-toluenesulphonylbenzoxazolone, m.p. 141—142°. (II) and ClCO_2Ph in $\text{C}_5\text{H}_5\text{N}$ afford unchanged material and *Ph* 5-bromo-3-*p*-toluenesulphonamido-*p*-tolyl carbonate whereas in warm dioxan containing NPhMe_2 the product is 6-bromo-2-*p*-toluenesulphonyl-4-methylbenzoxazolone, m.p. 175—176°. Under various conditions 5-bromo-3-amino-*p*-tolyl *p*-toluenesulphonate and ClCO_2Ph afford the diacyl derivative, m.p. 129—131°, and (by loss of PhOH) 1:3-di-(5-bromo-6-*p*-toluenesulphonoxy-3-methylphenyl)uretidone, m.p. 208—209°, hydrolysed to the $(\text{OH})_2$ -compound, $\begin{smallmatrix} \text{NR}\cdot\text{CO} \\ \text{CO}\cdot\text{NR} \end{smallmatrix}$ ($\text{R} = 2:5:3\text{-OH}\cdot\text{C}_6\text{H}_2\text{MeBr}$), m.p. 170° (decomp.).

H. W.

Relationships between constitution and action of derivatives of *p*-aminophenol. C. ROHMANN and K. FRIEDRICH (Ber., 1939, 72, [B], 1333—1339).— $\text{NEt}_2\cdot[\text{CH}_2]_2\text{Cl}$, HCl , and $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{ONa}$ in xylene at 135—145° give *p*-nitrophenyl β -diethylaminoethyl ether, decomp. >240° (yield 67%), reduced by Fe and HCl with a little Pt as catalyst to the NH_2 -derivative (I), which condenses with PhCHO in presence of ZnCl_2 to the :CHPh compound, reduced by Na and abs. EtOH at room temp. to *p*-benzylaminophenyl β -diethylaminoethyl ether (non-cryst. dihydrochloride). Condensation of (I) with the requisite aldehyde followed by reduction of the product gives the non-cryst. dihydrochlorides of *p*-ethylamino-, *p*-propylamino-, and *p*-*n*-butylamino-phenyl β -diethylaminoethyl ether. The compounds do not disturb the circulation and are non-irritant; they have a distinct local anaesthetising action.

H. W.

Synthesis of organic compounds containing radioactive sulphur. H. K. ALBER (J. Franklin Inst., 1939, 228, 177—181).— ^{35}S is prepared as a by-product of bombardment of CCl_4 with neutrons (cyclotron), mixed with (added) ^{32}S , and used to prepare radioactive ($\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}$)₂ (I) from $\text{p-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, Na_2S , and S , and thence by $\text{Cl}_2\cdot\text{H}_2\text{O}$ radioactive $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$. When ordinary or radioactive (I) is heated on a micro-m.p. hot stage, some (? tetragonal) crystals melt at 134°, resolidify and remelt at 164—165°, whereas the remaining crystals melt at 178—179° (lit. m.p. between 170° and 180°); three cryst. modifications are present.

R. S. C.

Hydroxyaryl alkyl and aralkyl sulphides.—See B., 1939, 808.

Normal and abnormal reactions of the sodium derivatives of aromatic thiols with halogenonitro-naphthalenes and -benzenes. H. H. HODGSON and E. LEIGH (J.C.S., 1939, 1094—1096).—Normal reactions of ArSNa with aromatic chloronitro-compounds support the explanation previously offered for the anomalous reactions (A., 1938, II, 406). PhSH and 2:1- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{NO}_2$ in hot $\text{NaOH}\cdot\text{EtOH}$ give *Ph* 1-nitro-2-naphthyl sulphide, m.p. 58—58.5°. *Ph* 4-nitro-1-naphthyl sulphide, m.p. 105.5—106°, is similarly prepared. The appropriate naphthyl- or anthraquinonyl-thiol with 2:1- or 1:4- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{NO}_2$ in hot $\text{NaOH}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ yields α -, m.p. 107°, and β - C_{10}H_7 1-nitro-2-naphthyl sulphide, m.p. 91°, α -, m.p. 127°, and β - C_{10}H_7 4-nitro-1-naphthyl sulphide, m.p. 151°, 1-nitro-2-, m.p. 435° (decomp.; block), and (?) 4-nitro-1-naphthyl 1-anthraquinonyl sulphide, decomp. when heated, 1-nitro-2-, m.p. 384° (decomp.; block), and (?) 4-nitro-1-naphthyl 2-anthraquinonyl sulphide, m.p. 238° (block).

R. S. C.

Activity of the methylene group in the isomeric *p*-tolyl mononitrobenzyl sulphones and in *p*-tolyl 2:4-dinitrobenzyl sulphone. R. L. SHRINER and S. O. GREENLEE (J. Org. Chem., 1939, 4, 242—251).—Interaction of $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Na}$ with the requisite nitrobenzyl halide in boiling EtOH affords *p*-tolyl *o*-, (I), m.p. 131—132°, *p*-, (II), m.p. 188—189°, and *m*-, (III), m.p. 160—161°, -nitrobenzyl sulphone and *p*-tolyl 2:4-dinitrobenzyl sulphone (IV), m.p. 159—160°. (I) and (II) are converted by NaOEt into coloured salts which do not alkylate with MeI or couple with I but are brominated to *p*-toluenesulphonyl-*o*-, m.p. 116—117°, and -*p*-, m.p. 166—167°, -nitrophenylmethyl bromide, respectively. (I) in PhNO_2 is converted by the successive action of $\text{KOEt}\cdot\text{EtOH}$ and I into *p*-toluenesulphonyl-*o*-nitrophenylmethyl iodide, m.p. 145—146°. (III) does not undergo bromination in presence of NaOEt . (IV) in PhNO_2 is transformed by $\text{KOEt}\cdot\text{EtOH}$ into a purple, cryst. salt (V), $\text{C}_{14}\text{H}_{11}\text{O}_6\text{N}_2\text{SK}$, from which the initial material is regenerated on acidification and which is brominated to *p*-toluenesulphonyl-2:4-dinitrophenylmethyl bromide, m.p. 178—180°. The halogeno-compounds give only a slight ppt. when boiled with $\text{AgNO}_3\cdot\text{EtOH}$ but the halogen is readily removed when they are boiled with NaOAc in 80% EtOH or by reduction with Na_2S . MeI converts (V) into α -*p*-

toluenesulphonyl- α -2:4-dinitrophenylethane, m.p. 167–168°, in 63% yield. I and (V) give $\alpha\beta$ -di-(*p*-toluenesulphonyl-2:4-dinitrophenyl)ethane, decomp. 375° (block). All these reactions indicate that the anion of the salt involved in these reactions is a carbanion and not one of the possible tautomeric *aci*-NO₂ structures. Boiling NaOH–EtOH converts *p*-nitrophenyl benzyl sulphone into 4:4'-dibenzylsulphonylazoxybenzene, m.p. 340–342°. *p*-C₆H₄Me·SO₂·CH₂·NO₂ (VI) gives a nearly colourless salt, C₇H₆O₄NSK. Addition of Br to (VI) in NaOH yields dibromonitro-*p*-toluenesulphonylmethane, m.p. 127°. Attempts to condense (I), (II), (III), (IV), or (VI) with Et₂C₂O₄ in presence of NaOEt or KOEt were unsuccessful; they could not be condensed with PhCHO.

H. W.

Functional aptitude of the methyl group. III. Derivatives of diphenyl sulphone.

L. CHARDONNENS and J. VENETZ (Helv. Chim. Acta, 1939, 22, 853–868).—In suitable conjunction with NO₂, Me appears to be more strongly activated by PhSO₂ than by Bz but two PhSO₂ groups are ineffective. 3:4-NO₂·C₆H₃Me·SO₂Cl, m.p. 36°, is transformed by AlCl₃ and C₆H₆ at 70° into 3-nitro-4-methyldiphenyl sulphone, m.p. 117.5°, which is converted by PhCHO in presence of piperidine at 130° into 3-nitro-4-styryldiphenyl sulphone, m.p. 191–192° (dibromide, decomp. 217°), by *p*-NMe₂·C₆H₄·CHO into 3-nitro-4-*p*-dimethylaminostyryldiphenyl sulphone, m.p. 177°, by *p*-OMe·C₆H₄·CHO into 3-nitro-4-*p*-methoxystyryldiphenyl sulphone, m.p. 158°, and by *p*-NO·C₆H₄·NMe₂ in boiling EtOH containing anhyd. Na₂CO₃ into 2-nitro-4-benzenesulphonylbenzal-*p*'-dimethylaminoanil, m.p. 187–188°, hydrolysed by HCl to 2-nitro-4-benzenesulphonylbenzaldehyde (I), m.p. 133–134° (phenylhydrazone, m.p. 217°; semicarbazone, m.p. 259°). *p*-C₆H₄Me·SO₂Ph is converted by conc. H₂SO₄ and HNO₃ (*d* 1.5) at 0–10° into 3:3'-dinitro-, m.p. 150–151°, and by conc. H₂SO₄ and HNO₃ (*d* 1.52) at room temp. and then at 100° into 3:5:3'-trinitro-, m.p. 191–192°, 4-methyldiphenyl sulphone. (I) is converted by 1% NaOH in aq. COMe₂ into 6:6'-dibenzenesulphonylindigotin, m.p. >370° (block). Similarly, 3:3'-dinitro-4:4'-dimethyldiphenyl sulphone affords 3:3'-dinitro-4:4'-distyryl-, m.p. 276° (block), and -4:4'-di-*p*-dimethylaminostyryl-, m.p. 237°, -diphenyl sulphone. The di-*p*-dimethylaminoanil, m.p. 250–251° (hydrolysed by HCl–H₂O in presence of CHCl₃), of 3:3'-dinitro-4:4'-diformyldiphenyl sulphone, m.p. 191–192° (disemicarbazone, m.p. >330°), is prepared. From 5-nitro-2-methyldiphenyl sulphone are derived 5-nitro-2-styryl-, m.p. 233°, and -2-*p*-dimethylaminostyryl-, m.p. 264°, -diphenyl sulphone and 4-nitro-2-benzenesulphonylbenzal-*p*'-dimethylaminoanil, m.p. 232.5°, hydrolysed to 4-nitro-2-benzenesulphonylbenzaldehyde, m.p. 121–122° (phenylhydrazone, m.p. 255–256°). 2:4-Dibenzenesulphonyltoluene, m.p. 192–193°, is conveniently prepared by heating 1:2:4-C₆H₃Me(SO₃H)₂ with C₆H₆ and P₂O₅ at 180°, or by transforming *p*-C₆H₄Me·SO₂Ph by a mol. proportion of ClSO₃H into PhSO₂·C₆H₃Me·SO₃H, which is heated with C₆H₆ and P₂O₅ at 180°; it does not condense with PhCHO. If *p*-C₆H₄Me·SO₂Ph is treated with a large

excess of ClSO₃H 4-methyldiphenyl sulphone-3:3'-disulphonyl chloride, m.p. 159°, appears to be formed.

H. W.

Manufacture of di-*p*-aminophenyl sulphones.—See B., 1939, 808.

Identification of aromatic sulphones. C. A. BUEHLER and J. E. MASTERS (J. Org. Chem., 1939, 4, 262–265).—Ph *p*-tolyl, *pp*'-ditolyl, *p*-chlorophenyl *p*-tolyl, and *p*-bromophenyl *p*-tolyl sulphone are oxidised (CrO₃ in glacial AcOH) to Ph *p*-carboxyphenyl, m.p. 266–268° (Et ester, m.p. 70–70.5°), di-*p*-carboxyphenyl, m.p. 358–363° (Et₂ ester, m.p. 156–156.5°), *p*-chlorophenyl *p*-carboxyphenyl, m.p. 274.1–275.3° (Et ester, m.p. 132–133°), and *p*-bromophenyl *p*-carboxyphenyl, m.p. 283.8–285.5° (Et ester, m.p. 133–134°), sulphone, respectively. The m.p. are high and insufficiently characteristic of the acids, which are therefore esterified by EtOH and conc. H₂SO₄. The (NO₂)₂-derivatives are obtained by the action of conc. HNO₃ and conc. H₂SO₄ at 60° on the sulphone and are highly characteristic. The following sulphones are described (all m.p. are corr.): di-*m*-nitrophenyl, m.p. 202.1–203.1°; ? *m*-nitrophenyl 2-nitro-*p*-tolyl, m.p. 151.7–152.7°; ? *m*-nitrophenyl 3-nitro-4-ethylphenyl, m.p. 137.7–138.8°; *m*-nitrophenyl 4-chloro-3-nitrophenyl, m.p. 146.6–147.6°; ? *m*-nitrophenyl 4-bromo-3-nitrophenyl, m.p. 162.1–163.1°; di-(2-nitro-*p*-tolyl), m.p. 164.2–165.2°; ? 2-nitro-*p*-tolyl 3-nitro-4-ethylphenyl, m.p. 116.4–117.4°; 4-chloro-3-nitrophenyl 2-nitro-*p*-tolyl, m.p. 151.2–151.7°; ? 4-bromo-3-nitrophenyl 2-nitro-*p*-tolyl, m.p. 160.1–161.1°; ? di-4-bromo-3-nitrophenyl, m.p. 235.3–237.3°.

H. W.

Crystalline esters of vitamin-A.—See A., 1939, III, 601.

Resolution of phenylmethylcarbinol. E. DOWNER and J. KENYON (J.C.S., 1939, 1156).—dl-CHPhMe H phthalate is resolved by brucine into the *l*-, m.p. 86°, [α]_D²⁰ –54.2° in CS₂, +30.2° in EtOH, [α]_D²⁵ –138.2° in CS₂, +96.4° in EtOH [other [α] also given; brucine salt, m.p. 153° (decomp.)], and *d*-form, [α]_D²⁵ +79.1° in CS₂. α for *l*-CHPhMe·OH, b.p. 93°/14 mm., for 5 λ are recorded. R. S. C.

Dehydration of α -phenyl- β -propenyl glycol. Formation of aldehyde (hydrobenzoin change) and ketone. Y. DEUX and D. ABRAGAM (Compt. rend., 1939, 208, 2084–2086; cf. Tiffeneau and Weil, A., 1937, II, 225; Deux, following abstract).— α -Phenyl- Δ^2 -pentene- $\alpha\beta$ -diol (I) (1 part) in 30% H₂SO₄ (5 parts) when distilled in steam gives a volatile oil (A), b.p. 139–141°/13 mm.; fractional crystallisation of the derived semicarbazones shows the presence of CHMe·CH·CHPh·CHO (II) or CHEt·CPh·CHO (III), and benzyl propenyl ketone (IV). Reduction of (A) (H₂–catalyst) gives a product, oxidised by Ag₂O to CHPhPr·CO₂H [from (II) or (III)] and COPr·CH₂Ph [from (IV)]. (II) or (III) is formed as a result of a hydrobenzoin change, whereas (IV) results from a vinyl mechanism. The aromatic character of propenyl is thus less marked than that of vinyl.

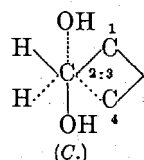
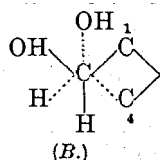
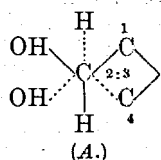
J. L. D.

Dehalogenation of α -phenyl- β -propenyl glycol iodohydrin and isomerisation of the corre-

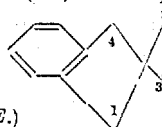
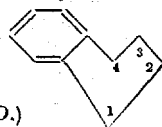
sponding oxide. Y. DEUX (Compt. rend., 1939, 208, 2002—2004; cf. A., 1939, II, 265).—CHPh:CH·CHET·OH (from CHPh:CH·CHO and MgEtBr) with hot H_2SO_4 gives α -phenyl- $\Delta^{\alpha\gamma}$ -penta-*diene* (I), b.p. 110—111°/14 mm., which with HgO and I in Et_2O - H_2O followed by treatment with AgNO_3 is converted into CHMe:CH·CHPh:CHO (II) or CHET:CPH:CHO (III), b.p. 142—143°/14 mm. (*semicarbazone*, m.p. 166—167°), so that propenyl behaves like an aromatic radical. (II) or (III) with H_2 -Raney Ni gives CHPhPr^a:CHO, oxidised to α -phenylvaleric acid, m.p. 53°. HOI adds to the double linking near Ph; dehalogenation is accompanied by a hydrobenzoin change. The chlorohydrin of (I) with powdered KOH gives α -oxido- α -phenyl- Δ^{γ} -pentene, b.p. 87—89°/4 mm., which under 20 mm. over kieselguhr at 250—300°, similarly gives (II) or (III).

J. L. D.

2 : 3 - Dihydroxytrans-decahydronaphthalenes and the configuration of tetrahydronaphthalene. K. GANAPATHI (Ber., 1939, 72, [E], 1381—1386; cf. A., 1938, II, 286, 496).—2 : 3-Diketotrans-decahydronaphthalene is reduced by Na-Hg to 2 : 3-dihydroxytrans-decahydronaphthalene (I), m.p. 141°, by Hg-Al in moist Et_2O to the isomeride (II), m.p. 128—129°, and by Al-Hg in EtOH to a mixture of (II) and the isomeride (III), m.p. 166°. Δ^2 -Octahydronaphthalene is oxidised by neutral KMnO_4 to (I) with a little (II) and by BzO_2H to an oxido-compound which is hydrolysed to (III). It follows therefore that (III) is *trans*-2 : 3-dihydroxytrans-decahydronaphthalene whereas (I) and (II) are *cis*-derivatives. (I) and (III) are unaffected by dry COMe_2 containing conc. H_2SO_4 whereas (II) is quantitatively isomerised to (III). (I), (II), and (III) have the configuration (A), (B), and (C), respectively. Titration of (I)—(III) with $\text{Pb}(\text{OAc})_4$ confirms the above views. The fact



that among the 2 : 3-dihydroxydecahydronaphthalenes the formation of COMe_2 derivatives is possible only when the two rings are united in the *cis* position to one another gives a ready method of determining the nature of the union of two rings of unknown configuration. The planar configuration of tetrahydronaphthalene is excluded by the Raman spectrum. The three 2 : 3-dihydroxytetrahydronaphthalenes have m.p. 135° (IV), 120° (V), and 140° (VI). The mixture of glycols obtained from 2 : 3-dibromotetrahydronaphthalene is converted by COMe_2 and 1% HCl into (IV) and the COMe_2 derivative (VII) of (V). It appears therefore that (IV) is the *trans*-isomeride produced by the isomerisation of (VI). The produc-



tion of (VII) shows that in (V) the OH groups lie in the same plane as the C atoms to which they are

united. The tetrahydronaphthalene ring, at any rate as far as its 2 : 3-(OH)₂-derivative is concerned, has the spatial configuration (D) and not (E). The *disemicarbazone* of *trans*-cyclohexane-1 : 2-diacetaldehyde has m.p. 160—162°. H. W.

Influence of the structure of bromo-derivatives of alkyl- and alkoxy-benzenes on the synthesis of pinacols by the Grignard method. T. W. JEZERSKI (Rocz. Chem., 1939, 19, 307—316).—The following 9 : 10-dihydroxy-9 : 10-diaryl-9 : 10-dihydrophenanthrenes were synthesised from phenanthraquinone and MgRBr, under identical conditions (yields given in parentheses): aryl = *o*-tolyl, m.p. 151.5—152° (51%), *m*-tolyl (45%), *p*-tolyl (57%), 3 : 4-dimethylphenyl, m.p. 194.5—195° (23%), *o*-anisyl, m.p. 179—180° (43%), *m*-anisyl, m.p. 185.5—186.5° (48%), *p*-anisyl (47%), *o*-phenetyl, m.p. 196—197° (52%), *m*-phenetyl, m.p. 159—160° (39%), and *p*-phenetyl (44%); Mg *m*-4- and *p*-xylol bromides do not give the expected derivatives. The above products are oxidised (CrO_3) to 2 : 2'-diaroyldiphenyls, viz., *di*-*o*-toluoyl, m.p. 134.5—135.5° (79%), *m*-toluoyl (71%), *p*-toluoyl (72%), 3 : 4-dimethylbenzoyl, m.p. 126—127° (52%), *o*-anisoyl, m.p. 136—137° (84%), *m*-anisoyl, m.p. 87—88° (90%), *p*-anisoyl (83%), *o*-ethoxybenzoyl, m.p. 142.5—143.5° (70%), *m*-ethoxybenzoyl, m.p. 91.5—92.5° (82%), and *p*-ethoxybenzoyl (75%). R. T.

Oxidation of adrenaline by succinic acid. Inhibition by cocaine and sparteine. T. WENSE (Z. physiol. Chem., 1939, 260, 100—104; cf. Marquardt, A., 1939, III, 581).—Tests with luminol and a trace of haemin show that aq. succinic (I) and fumaric acid contain peroxide which is probably responsible for the inactivation of adrenaline by solutions of these acids. The degree of luminescence is not increased by exposing the solutions of the acids to sunlight. The action of (I) is not increased by ergotamine. The oxidation of adrenaline by the solutions is inhibited by cocaine and sparteine. Sparteine (but not cocaine) also inhibits the autoxidation of adrenaline and the inactivation of adrenaline by MeCHO. Cocaine diminishes but sparteine increases the luminescence produced with luminol. W. McC.

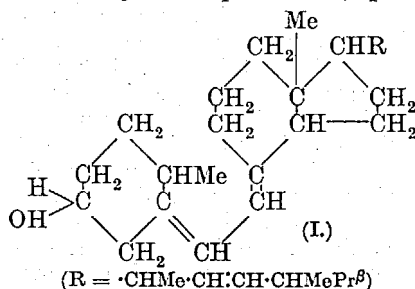
Biochemical reduction of a 1 : 2-benzanthracene derivative. A. DANSI and A. VERCELLONE (Ber., 1939, 72, [E], 1457—1458).—1 : 2-Benzanthracene-10-aldehyde is reduced by fermenting yeast to 10-hydroxymethyl-1 : 2-benzanthracene, m.p. 173—174°. H. W.

[Sensitive test for ergosterol and differentiation of ergosterol and ergosteryl esters.] A. F. VON CHRISTIANI and V. ANGER (Ber., 1939, 72, [B], 1482; cf. A., 1939, II, 316).—The indicated concn. of $\text{Pb}(\text{OAc})_4$ is double that required. H. W.

Catalytic hydrogenation of cholesteryl acetate in acetic acid containing hydrochloric acid. T. KAWASAKI (J. Pharm. Soc. Japan, 1939, 59, 79—80).—Hydrogenation (Pt-black) of cholesteryl acetate in AcOH-38% HCl (34 : 1) gives, through the acetate, cholestanol, m.p. 140—141° when purified chromatographically (C_6H_6 solution; activated Al_2O_3); a small amount of cholestane is formed also (probably through cholesterylene). A. T. P.

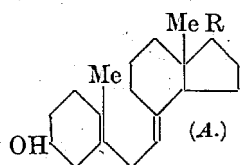
Sitosterol complex. Isolation of α_3 -sitosterol. S. BERNSTEIN and E. S. WALLIS (J. Amer. Chem. Soc., 1939, 61, 1903—1904).—Wheat-germ oil yields α_1 -, α_2 -, and a little α_3 - (I) -sitosterol (cf. Wallis *et al.*, A., 1937, II, 100). (I), $C_{29}H_{48}O$, m.p. 142—143°, $[\alpha]_D^{20} +5.2^\circ$, gives a benzoate, m.p. 173—175°, $[\alpha]_D^{20} +12.0^\circ$, 3:5-dinitrobenzoate, m.p. 210—211.5°, $[\alpha]_D^{20} +12.2^\circ$, and acetate, m.p. 152—153°, $[\alpha]_D^{20} +6.1^\circ$ (all $[\alpha]$ in $CHCl_3$). R. S. C.

Dihydrotachysterol. F. VON WERDER (Z. physiol. Chem., 1939, 260, 119—134; cf. Windaus *et al.*, A., 1933, 62).—The product (A) obtained by reduction (Na, EtOH) of tachysterol contains ~30% of the antirachitically inactive dihydrovitamin- D_2 (cf. Windaus *et al.*, A., 1932, 311), m.p. 65—66°, $[\alpha]_D^{25} +10^\circ$ (all rotations in $CHCl_3$) (benzoate, m.p. 70—71°, $[\alpha]_D^{25} +30^\circ$), separable as the allophanate, m.p. 184—186°, $[\alpha]_D^{25} +16^\circ$, and also obtained by similar reduction of vitamin- D_2 . The fraction of (A) not, or only slightly, adsorbed on Brockmann's Al_2O_3 consists largely of dihydrotachysterol (I), m.p. 125—127°, $[\alpha]_D^{25} +97.5^\circ$ (propionate, m.p. 97—98°, $[\alpha]_D^{25} +37^\circ$; n-butyrate, m.p. 62—63°), purified chro-



matographically through the acetate (II), m.p. 108—110°, $[\alpha]_D^{25} +32.8^\circ$. (I) and its esters show characteristic absorption max. at 242, 251, and 261 mμ. (II) consumes 3 H_2 (Pt, 96% AcOH), does not react with $(CH_3CO)_2O$ in xylene at 135°, and is oxidised (CrO_3 , aq. AcOH, room temp.) to the ketone, $C_{19}H_{32}O$, of Windaus *et al.* (A., 1936, 1247). The antirachitic activity of (I) is ~0.5% of that of vitamin- D_2 ; (I) possesses the highest calcification factor of any substance (derived from irradiated ergosterol) so far investigated. The limiting toxic dose (mouse) of (I) and (II) is 10 and 200 μg. respectively. H. B.

Constitution of dihydrovitamin- D_2 and - D_3 . A. WINDAUS and C. ROOSEN-RUNGE (Z. physiol. Chem., 1939, 260, 181—184).—Oxidation (O_3 , AcOH) of the allophanate, m.p. 165°, $[\alpha]_D^{25} +61.3^\circ$ in $CHCl_3$, of dihydrovitamin- D_3 (I) gives the same ketone, $C_{18}H_{32}O$, as is obtained from vitamin- D_3 (A., 1938, II, 58). Dihydrovitamin- D_2 (II) is oxidised $[Al(OBu^t)_3, COMe_2, C_6H_6]$ to a ketone, the semicarbazone, $C_{29}H_{47}ON_3$, m.p. 208—210° (decomp.), of which shows



the characteristic high absorption (max. at 270 mμ.) of an $\alpha\beta$ -unsaturated ketone. (I) and (II) are, therefore, most probably (A) with R = $-CHMe·[CH_2]_3·Pr^β$ and $-CHMe·CH·CH·CHMePr^β$, respectively (cf. *loc. cit.*; von Reichel *et al.*, A., 1936, 603). H. B.

Sterols. XIV. Ketone cyanohydrins. S. KAWADA and M. MIYASAKA (J. Pharm. Soc. Japan, 1938, 58, 115—118; cf. A., 1937, II, 190).—Androsterone and isoandrosterone afford cyanohydrins, decomp. 163° (diacetate, m.p. 183°) and 210° (diacetate, m.p. 144°), respectively. *trans*-Dehydroandrosterone cyanohydrin diacetate and $MgMeI$ afford 17-methyl- $\Delta^{5:6}$ -*trans*-androsterone-3:17-diol, m.p. 197—199° (diacetate, m.p. 146°), identical with that from *trans*-dehydroandrosterone and $MgMeI$. Cholestanone cyanohydrin, decomp. 125—150°, and $MgMeI$ give 3-methyl-, m.p. 147—148° [with a (?) stereoisomeride, m.p. 125°; both dehydrated (Ac_2O ; Bu^tCO_2H ; $C_5H_5N-Ac_2O$) to 3-methyl- Δ^{2or3} -cholestene], and 3-acetyl-cholestan-3-ol, m.p. 173° (purified through the semicarbazone, m.p. ~250°). A. T. P.

Estradiol 3- CH_2Ph ether, m.p. 82—84°.—See B., 1939, 885.

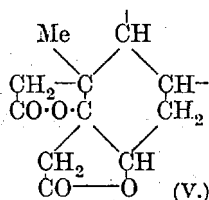
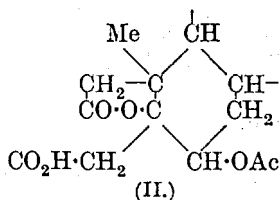
Sterols. LXVIII. Highly branched aliphatic esters of oestrone and α -estradiol. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 1922—1923).—*Estrone* 3- α -dimethylpropionate, m.p. 164—166° [hydrogenated (PtO_2 ; $EtOH-Et_2O$) to α -estradiol 3- α -dimethylpropionate, m.p. 178—180°], and 3- β -dimethyl-n-butyrate, m.p. 148—150° (hydrogenated to α -estradiol 3- β -dimethyl-n-butyrate, m.p. 127—129°), α -estradiol 3:17-bis- α -dimethylpropionate, m.p. 174—176°, and 3:17-bis- β -dimethyl-n-butyrate, m.p. 98—100°, are prepared. R. S. C.

Estradiol 3-acylates.—See B., 1939, 885.

Sugar-cane wax. III. New constituents of unsaponifiable fraction. T. MITUI (J. Agric. Chem. Soc. Japan, 1939, 15, 526—530; cf. A., 1938, II, 232).—The unsaponifiable fraction also contains α -saccharostanediol (I), $C_{29}H_{52}O_2$, m.p. 206° (dibenzoate, m.p. 160°; di-3:5-dinitrobenzoate, m.p. 171°), and β -saccharostenone (II), $C_{29}H_{48}O$, m.p. 106° (oxime, m.p. 163—165°; 2:4-dinitrophenylhydrazones, m.p. 206°; tribromide, m.p. 160.5°). (I) contains 2 OH whilst (II) contains 1 CO and 1 double linking. J. N. A.

Steroids and related compounds. IV. Stereochemical configuration of the cholestane-3:5:6-triols. B. ELLIS and V. A. PETROW (J.C.S., 1939, 1078—1083; cf. A., 1939, II, 367).—The triol obtained from cholesterol by H_2O_2 , now renamed cholestane-3:5:6-triol-I, is shown by the following and Criegee's evidence (A., 1933, 62) to be the 3(β):5(α):6(β)-triol. The isomeric cholestane-3:5:6-triol-II (new name) (obtained by $KMnO_4$ or OsO_4) is similarly shown to be the 3(β):5(β):6(β)-triol. The arguments are based on the rules of bromination and oxidative ring-fission for 3-ketosteroids being unaffected by the OH on C_{15} . 3:6-Diacetoxycholestan-5-ol with cold KOH-abs. EtOH gives 6-acetoxycholestan-3:5-diol, $+H_2O$, m.p. 132—133° or (anhyd.) 143—144°, $[\alpha]_D^{19} -26.4^\circ$, converted by $BzCl-C_5H_5N$ into the known 3-benzoyloxy-6-acetoxycholestan-5-ol and by CrO_3 in AcOH at 100° (3 min.) into 6-acetoxycholestan-5-ol-3-one (I), m.p. 161—162°, $[\alpha]_D^{19} -10.2^\circ$, and the 6-acetoxy-lactonic acid (II), $C_{29}H_{46}O_6$, m.p. 217—218° (sinters at 185°), $[\alpha]_D^{20} -10.4^\circ$. $SOCl_2-C_5H_5N$, first at room temp.

and then boiling, or boiling Ac_2O dehydrates (I) to 6-acetoxy- Δ^4 -cholesten-3-one (III), m.p. 101.5° , $[\alpha]_D^{25} +36^\circ$, hydrolysed by 1% KOH - MeOH at room temp. to Δ^4 -cholesten-6-ol-3-one (IV), m.p. 192° (known semicarbazone, m.p. 221°), which is oxidised by CrO_3 in C_6H_6 - AcOH to the known Δ^4 -cholesten-3:6-dione. HCl - EtOH converts (III) or (IV) into cholestan-3:6-dione, also obtained from (III) by 5% NaOMe - MeOH (excess). 0.5% KOH - EtOH converts (II) into the dilactone (V), $\text{C}_{27}\text{H}_{42}\text{O}_4$, m.p. 165° (sinters at 155°) (neutralises 2 KOH hot). With Br in AcOH at 35° , (I) gives 2-bromo- (VI) (40%), m.p.



186° , $[\alpha]_D^{25} +3.6^\circ$, and a little 2:2-dibromo-6-acetoxycholestan-5-ol-3-one, m.p. 218° (decomp.), $[\alpha]_D^{25} +70.9^\circ$ [obtained also by further bromination (presence of a trace of HBr) of (VI); with NaI in C_6H_6 - EtOH liberates Br]. $\text{C}_5\text{H}_5\text{N}$ is without effect on (VI), but 1.5% KOH - MeOH at 55 – 60° converts it into cholestan-6-ol-3-one 2:5-oxide (20–30%), m.p. 181 – 182° (stable to 10% HCl - EtOH ; acetate, m.p. 84° , regenerates the oxide with 2.5% KOH - MeOH), which with CrO_3 - AcOH gives cholestan-3:6-dione 2:5-oxide, m.p. 115 – 116° (bis-2:4-dinitrophenylhydrazones, m.p. 171°). Cholestan-3:5-diol-6-one belongs to the triol-II series, since CrO_3 - AcOH oxidises it to coprostan-5(β)-ol-3:6-dione [= cholestan-5-ol-3:6-dione-II]. Partial CrO_3 -oxidation of triol-I at room temp. gives a product, converted by boiling Ac_2O into 3-acetoxycholestan-5-ol-6-one (VII), m.p. 238° , $[\alpha]_D^{25} -56.2^\circ$. NaOMe - MeOH hydrolyses (VII) to cholestan-3:5-diol-6-one-I (VIII), and SOCl_2 in hot $\text{C}_5\text{H}_5\text{N}$ dehydrates it to 3(β)-acetoxy- Δ^4 -cholesten-6-one. Ac_2O - KHSO_4 at 100° or boiling Ac_2O converts (VII) into 3(β):5(α)-diacetoxycholestan-6-one, m.p. 169 – 170° , $[\alpha]_D^{25} -11^\circ$, hydrolysed to (VIII). M.p. are corr. $[\alpha]$ are in CHCl_3 . R. S. C.

Chaulmoogryl chaulmoograte. T. KARIYONE and T. SUGAHARA (J. Pharm. Soc. Japan, 1939, 59, 18–20).—Reduction of chaulmoogra oil (I) by Na and EtOH gives a mixture separated by fractional distillation into hydnocarpyl alcohol, b.p. 136 – $142^\circ/1$ mm., m.p. 19° , $[\alpha]_D^{17} +56.27^\circ$ (phenylurethane, m.p. 69°), and chaulmoogryl alcohol (II), b.p. 152 – $158^\circ/1$ mm., m.p. 23° , $[\alpha]_D^{17} +57.90^\circ$. When hydrogenated in presence of Ni , (I) affords dihydrohydnocarpyl alcohol, b.p. 155 – $165^\circ/2$ mm., m.p. 25° (phenylurethane, m.p. 72°), and dihydrochaulmoogryl alcohol, b.p. 155 – $160^\circ/1.5$ mm. Chaulmoogryl chloride and (II) give chaulmoogryl chaulmoograte, m.p. 31° , $[\alpha]_D^{25} +55.40^\circ$ in CHCl_3 . H. W.

Derivatives of phenylacetonitrile. P. JULIEN (Bull. Soc. chim., 1939, [v], 6, 1252–1254; cf. A., 1936, 1109).— $\text{CH}_2\text{Ph}\cdot\text{CN}$ and Et_2O - NaNH_2 followed by BuBr give a mixture of Bu_1 and Bu_2 derivatives, further treated similarly to give $\text{CBu}_2\text{Ph}\cdot\text{CN}$, b.p. 172 – $175^\circ/25$ mm., hydrolysed by KOH - EtOH at

100° (bath) to a little $\text{CBu}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$, m.p. 76° . Similarly prepared is $\text{CPr}^2\text{Ph}\cdot\text{CN}$ (I), b.p. 144 – $146^\circ/25$ mm., separated from $\text{CHPr}^2\text{Ph}\cdot\text{CN}$ (II) by treating with 85% H_2SO_4 ; (I) is unaltered and (II) gives the corresponding amide. $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CN}$, m.p. 58° , and $(\text{CH}_2\text{Ph})_2\text{CPh}\cdot\text{CN}$, m.p. 83° , are readily prepared. A. T. P.

Kolbe's electrosynthesis with aromatic acids; benzoic, phenylacetic, β -phenylpropionic, and phenoxyacetic acid. F. FICHTER and H. STENZL (Helv. Chim. Acta, 1939, 22, 970–978).—Kolbe's electrosynthesis can be effected with various aromatic acids if $\text{C}_5\text{H}_5\text{N}$ is used as solvent; the films which so frequently form on the anode during electrolysis of solutions in H_2O or MeOH are thereby dissolved. The difficulty of effecting Kolbe's electrosynthesis with aromatic acids depends on the sensitiveness of the aromatic nucleus towards anodic O. The use of $\text{C}_5\text{H}_5\text{N}$ alone or in presence of MeOH prevents the evolution of O_2 at the anode. The new method has been applied successfully to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and with smaller yields to BzOH . With BzOH , 4-phenylpyridine and p - $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$ are formed as characteristic by-products in addition to Ph_2 . Both compounds are obtained by the thermal decomp. of Bz_2O_2 in $\text{C}_5\text{H}_5\text{N}$. It therefore appears that Bz_2O_2 is formed as intermediate product at the anode during electrolysis; similar results have been obtained by the electrolysis of fatty acids. With the other aromatic acids investigated, considerably better yields of the synthetic hydrocarbons are obtained. In all cases the formation of amorphous brown products and the evolution of CO are observed; an explanation cannot yet be given. $\alpha\delta$ -Di-(2:4-dinitrophenyl)butane, m.p. 204 – 205° , is prepared. H. W.

Acetonephenylpyruvic [α -hydroxy- γ -keto- α -benzylvaleric] acid and its dehydration product. P. CORDIER (Compt. rend., 1939, 209, 49–51; cf. A., 1938, II, 60).—The acid is easily dehydrated in AcOH - HCl to (probably) γ -keto- α -benzyl- Δ^2 -pentenoic acid, m.p. 94° , which when oxidised (NaOCl or NaOBr) gives benzyl-maleic (I) and -fumaric (II) acids (cf. A., 1928, 519). When excess of NaOH is removed with NaHSO_3 , more (II) is isolated, whereas As_2O_3 leads to (I). J. L. D.

Aldehyde-acids and aldo-enol-lactones. II. Synthesis of the γ -lactone of $\alpha\gamma$ -dihydroxy- β -phenyl- Δ^2 -butenoic acid (3-hydroxy-2-keto-4-phenyl-2:3-dihydrofuran). III. Certain specific properties of γ -aldo-enol-lactones and unsaturated aldehyde-acids. M. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1939, 9, 484–490, 491–495).—II. $\text{OH}\cdot\text{CH}(\text{OEt})\cdot\text{CO}_2\text{Et}$ and $\text{CH}_2\text{Ph}\cdot\text{CHO}$ in Ac_2O (20 hr. at 140 – 145°) yield 2-keto-3-acetoxy-4-phenyl-2:3-dihydrofuran (I), m.p. 140 – 141° , and the *Et* ester (II), b.p. 110 – $114^\circ/3$ mm. (semicarbazone, m.p. 167°), of β -aldehyde- β -phenylacrylic acid, m.p. 161 – 162° [also obtained by hydrolysis with 10% HCl of (I)].

III. (I) or (II) and 3% NaOH at 80 – 90° yield a truxinic acid, m.p. 195 – 196° (*Me* ester, m.p. 198 – 199°), differing from other known truxinic acids.

R. T.

Naphthylacrylic acids and their derivatives.

I. β -2-Naphthylcrotonic acids. A. BANCHETTI (Gazzetta, 1939, 69, 398—405).— β -C₁₀H₇·COMe (I) and CH₂Br·CO₂Et with Zn in boiling C₆H₆ give the Et ester (II), b.p. 210—215°/24 mm., of β -2-naphthylcrotonic acid (III), m.p. 169—170° (product, m.p. 140—150°, with Br₂), to which, with other substances, (II) is hydrolysed by KOH-EtOH. With conc. H₂SO₄, (II) gives (I), not an indone. Aq. KMnO₄-Na₂CO₃ oxidises (III) to (I). A solution of (III) in C₆H₆ exposed to ultra-violet light yields a stereoisomeride, m.p. 141—142°. Either this or (III) is reduced by Na-Hg in aq. NaOH to β -2-naphthylbutyric acid, m.p. 109—110°. E. W. W.

Chemistry and metabolism of phenylalanine.

I. Nitration. R. J. BLOCK and D. BOLLING (J. Biol. Chem., 1939, 129, 1—12).—The view that the violet colour formed in the colorimetric determination of phenylalanine (I) is due to a derivative of diaci-o-dinitrodihydrobenzene is confirmed by the prep. of diaci-3:4-dinitro-3:4-dihydrophenylalanine (II), m.p. 182—183° (decomp.), giving a negative ninhydrin reaction, by nitration of (I) with conc. H₂SO₄ containing Ba(NO₃)₂ at 100° followed by reduction by H₂S. It gives the typical violet colour on treatment with aq. NH₃, NaOH, or Na₂CO₃ (p_H ~9.5). 3:4-Dinitrophenylalanine, m.p. 155°, decomp. 182°, has also been prepared. The cherry-red colour produced by nitration of BzOH followed by reduction is probably formed from 2:5-(NO₂)₂C₆H₃·CO₂H. Reduction of all derivatives of p -C₆H₄(NO₂)₂ yields a red colour, and of o -C₆H₄(NO₂)₂ a violet colour. The mechanism of these reactions is discussed. (II) is accompanied by a red amorphous solid, decomp. 220—250° (softens ~65—70°), which may be 3:4-dinitro-3:4-dihydrobenzoic acid.

P. G. M.

Azlacones. I. Preparation of α -benzamido-crotonic acid azlactone and the conversion of allothreonine into threonine. H. E. CARTER, P. HANDLER, and D. B. MELVILLE (J. Biol. Chem., 1939, 129, 359—369).— N -Benzoyl- dl -threonine, N -benzoyl- dl -allothreonine, and their O -Me, O -Ac, m.p. 138—140° and 86—89°, respectively, and -Bz, new m.p. 158—159° and 179—180°, respectively, derivatives are converted into α -benzamido-crotonic acid azlactone (I), m.p. 95—96°, by the action of BzCl in C₅H₅N. NaOMe converts (I) into N -benzoyl- O -methyl-threonine. The structure of (I) is confirmed by synthesis from hippuric acid and MeCHO, hydrolysis (π -HCl) to α -benzamido-crotonic acid, m.p. 193—195°, and EtCO·CO₂H, and reduction (H₂, PtO₂, AcOH) to NHBz·CH₂Et·CO₂H. E. M. W.

Derivatives of 4-chloro-3-nitrobenzonitrile.

C. H. D. WITTE (Diss., Leiden, 1939, 107 pp.).— p -Chloro- (m.p. 101°) and -bromo-benzonitrile give the 3-NO₂-derivatives on nitration and a second NO₂-group cannot be introduced directly. Nitration of p -cyano-anisole or -phenetole affords the 2-NO₂-derivative [also obtained from 3:4:1-NO₂·C₆H₃Cl·CN (I) and NaOMe or NaOEt] and 2:6-dinitro-4-cyano-anisole, m.p. 114°, or -phenetole respectively. The appropriate amine and (I) give N -methyl- (Ac derivative, m.p. 92°), -ethyl- (Ac derivative m.p. 85°), - n -

propyl-, m.p. 116° (Ac derivative, m.p. 102°), - n -butyl-, m.p. 69° (Ac derivative, m.p. 63°), - n -amyl-, m.p. 60°, - n -heptadecyl-, m.p. 82° (Ac derivative, m.p. 77°), and - β -hydroxyethyl- (II), m.p. 135° (N-Ac derivative, m.p. 130°), -2-nitro-4-cyano-anilines. N - n -Heptadecyl-2:4-dinitroaniline, m.p. 61° (Ac derivative, m.p. 70°), is obtained by interaction of C₁₇H₃₅NH₂ and 1:2:4-C₆H₃Cl(NO₂)₂. Nitration of (II) gives β -N-(2:6-dinitro-4-cyanophenyl)- N -nitro-aminoethyl nitrate, m.p. 130°, also obtained by nitrating N - β -hydroxyethyl-2:6-dinitro-4-cyanoaniline, m.p. 116°, prepared from ethanolamine and (I). Nitration of NN'-di-(2-nitro-4-cyanophenyl)ethylene-diamine, prepared from (CH₂NH₂)₂ and (I), or NN'-di-(2:6-dinitro-4-cyanophenyl)ethylenediamine, m.p. 282°, obtained by replacement of OMe in corresponding anisole, gives NN'-dinitro-NN'-di-(2:6-dinitro-4-cyanophenyl)ethylenediamine, m.p. 204° (block), 212° (tube). (I) reacts with N₂H₄ and NHMe·NH₂ forming 2-nitro-4-cyanophenyl-hydrazine and - α -N-methylhydrazine, m.p. 130°, respectively. 2-Nitro-4-cyanophenyl-hydrazones and -methylhydrazones of the following are described, the respective m.p. being given in parentheses: COMe₂ (128°, 144°); COMeEt (139°, 124°); COEt₂ (129°, 125°); CH₂O (175°, 126°); MeCHO (179°, 110°); EtCHO (132°, 129°); Pr'CHO (138°, 101°); PhCHO (225°, 183°); o - (255°, 218°), m - (272°, 209°), and p -NO₂·C₆H₄·CHO (301°, 235°); o - (276°, 191°), m - (256°, 173°), and p -C₆H₄Cl·CHO (253°, 193°); 3:4-CH₂O₂·C₆H₃·CHO (279°, 176°); 4-hydroxy-3-methoxy- (304°, 225°), and -3-ethoxy-benzaldehyde (308°, 237°); furfuraldehyde (204°, 184°); 5-methyl- (199°, 169°) and 5-hydroxymethyl-furfuraldehyde (177°, —). (I) reacts with Na₂S₂ forming 2:2'-dinitro-4:4'-dicyanodiphenyl disulphide; the product obtained with Na₂S is indefinite. The taste of the various compounds is discussed. S. C.

Nitroamines.

VIII. Nitroaminobenzoic acid. E. MACCIOTTA (Gazzetta, 1939, 69, 330—332).— o -NH₂·C₆H₄·CO₂H with HNO₃ (d 1.52) in AcOH gives o -nitroaminobenzoic acid (deflagrates when heated) (Na and Ag salts), which in conc. H₂SO₄ rearranges to 3:2:1-NO₂·C₆H₃(NH₂)·CO₂H. m -NH₂·C₆H₄·CO₂H similarly with HNO₃, followed by Hg(OAc)₂ gives Hg bis- m -nitroaminobenzoate.

E. W. W.

Chloral-chlorosalicylamides and their methyl ethers. N. W. HIRWE and K. N. RANA (Ber., 1939, 72, [B], 1346—1353; cf. A., 1939, II, 264).—In hydroxybenzamides the condensation with chloral is restricted partly by OH in the *ortho*- and completely by OH in the *meta*- or *para*-position. The condensation of methoxybenzamides is facilitated by OMe in the *ortho*-, *meta*-, or *para*-position. A negative group in position 3 (o to OH) in o -OH·C₆H₄·CO₂H favours condensation, which is restricted by a similar group at C₅ (p to OH). The following are obtained by heating a mixture of amide and chloral under an air condenser until a clear solution is obtained: chloral-3-chloro- (I) [3-chloro-2-hydroxybenz- $\beta\beta\beta$ -trichloro- α -hydroxyethylamide], m.p. 159—160°, -5-chloro- (II), m.p. 148—149° (decomp.), and -3:5-dichloro-, (III), m.p. 158—159° (decomp.), -salicylamide; chloral-3-

chloro-, m.p. 115—116°, *-5-chloro-* (IV), m.p. 157—158° (decomp.), and *-3:5-dichloro-*, m.p. 143—144°, *-2-methoxybenzamide*. Chlorination of chloralsalicylamide with Cl_2 (1 mol.) in AcOH at $>20^\circ$ gives mainly (I) with some (II) and 5-chlorosalicylamide, m.p. 226—227°; if two mols. of Cl_2 are used (III) is obtained. Similarly chloral-2-methoxybenzamide and Cl_2 (1 mol.) afford (IV), also obtained exclusively when more than 1 mol. of halogen is used.

H. W.

Synthesis of homoisovanillic acid. H. W. BERSCH (Arch. Pharm., 1939, 277, 271—286; cf. A., 1922, i, 569; Schöpf *et al.*, A., 1932, 1040).—O-Carboethoxyisovanillin, m.p. 58—59° [from isovanillin (I), ClCO_2Et , and dil. NaOH], with NaHSO_3 followed by NaCN yields the *cyanohydrin*, m.p. 98° (sinters at 90°), which with MeOH-HCl and then H_2O gives Me 3-carboethoxy-4-methoxymandelate. Successive chlorination (SOCl_2), reduction (H_2 , PtO_2 , $\text{C}_5\text{H}_5\text{N}$), and hydrolysis of this yields homoisovanillic acid, new m.p. 127—129° [30—40% yield from (I)]. Several other methods were tried. Vanillin and BzCl in Et_2O with aq. KCN yields O-benzoylvanillin *cyanohydrin benzoate*, m.p. 146.5—147.5, reduced (Pd in tetrahydronaphthalene) to 4-benzoyloxy-3-methoxyphenylacetone, m.p. 110°; O-benzoylisovanillin *cyanohydrin benzoate* (oil) is similarly prepared (poor yield). (I) with MeNO_2 yields ω -nitro-3-hydroxy-4-methoxystyrene, m.p. 155—156° (sinters at 150°), reduced (H_2 , Pd-C, $\text{C}_5\text{H}_5\text{N}$) to 3-hydroxy-4-methoxyphenylacetaldoxime, m.p. 146—147°. Acetylation (Ac_2O -conc. H_2SO_4) of (I) yields a mixture of the mono-, m.p. 86° , and tri-acetate, m.p. 117—118°. 3-Benzoyloxy-4-methoxybenzyl alcohol, m.p. 70—71° (from isovanillyl alcohol, CH_2PhCl , and MeOH-NaOMe), with SOCl_2 yields the *chloride*, m.p. 70—75°, which does not react normally with KCN. 3-Nitro-4-methoxyphenyl-acetonitrile, m.p. 86—87° (from the chloride and NaCN), is hydrolysed to the *-acetic acid*, m.p. 133—134° (sinters at 129°); reduction (H_2 , Pd-C, EtOAc) of the nitrile and of the *Me*, m.p. 102° , and *Et*, m.p. 58—59°, esters of the acid yields respectively 3-amino-4-methoxyphenylacetone, m.p. 40° (*hydrochloride*, m.p. 202°), and *Me*, b.p. 147—148°/1 mm. (*hydrochloride*, m.p. 190—191°), and *Et* 3-amino-4-methoxyphenylacetate, b.p. 150—152°/1 mm. [*hydrochloride*, m.p. 166—167° (turning brown)], none of which can be satisfactorily diazotised. α -Diethylamino- α -3:4-methylenedioxy- (cf. Knoevenagel, A., 1904, i, 982) and -3-hydroxy-4-methoxyphenyl-acetonitrile (similarly prepared), m.p. 83° (sinters at 78°), do not react with EtBr or MeI. A. Li.

Condensation of 4-nitro-*o*-tolunitrile with aromatic aldehydes. C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1939, [v], 6, 1182—1187; cf. A., 1938, II, 491).—4:1:2- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CN}$ (I) (unaffected by NaOMe-MeOH) and PhCHO or $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in NaOMe-MeOH afford 4-nitro-(II), m.p. 263° (partial decomp.), or 4:2'-dinitro-2-carbamylstilbene, m.p. 228° . (I) and PhCHO with piperidine at 130—140° give 4-nitro-2-cyanostilbene, new m.p. 145° (unaffected by NaOMe). The latter and H_2O_2 -MeOH, followed by aq. KOH to the boiling solution, give (II); (I) similarly affords 4:1:2-

$\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{NH}_2$, new m.p. 175° . The mechanism of reaction is discussed. A. T. P.

Hydrindene derivatives. II. Simple substitution products. J. LINDNER, F. SCHMITT, and B. ZAUNBAUER (Monatsh., 1939, 72, 216—222).—Directions are given for the conversion of 4 and 5-aminohydrindene into the corresponding hydroxy-, acetoxy-, methoxy-, and cyano-hydrindenes; the acids and their amides are described. 5-Acetoxyhydrindene, m.p. 17—18°, and hydrindene-4-carboxylic acid, m.p. 155° (amide, m.p. 171.5°), appear new.

H. W.

Synthesis of sphaerophorin. A. HASHIMOTO [with S. Koyama] (J. Pharm. Soc. Japan, 1938, 58, 221—223).—Sphaerophorol, HCl, HCN, and AlCl_3 give sphaerophorolaldehyde (I), 3:5:1:2-(OH) $_2\text{C}_6\text{H}_2(\text{C}_7\text{H}_{15})\cdot\text{CHO}$, m.p. 83° (p-nitrophenylhydrazones, m.p. 204°); its $\text{OO}\cdot(\text{CO}_2\text{Et})_2$ -derivative by KMnO_4 -oxidation and hydrolysis affords sphaerophorolcarboxylic acid, m.p. 140° . 5:1:3:2-OMe-C $_6\text{H}_2\text{Me}(\text{O}\cdot\text{CO}_2\text{Et})\cdot\text{COCl}$ and (I) in $\text{C}_5\text{H}_5\text{N}$ give the aldehyde (p-nitrophenylhydrazones, decomp. 182°) corresponding with sphaerophorin (II); treatment with $\text{ClCO}_2\text{Et}\cdot\text{C}_5\text{H}_5\text{N}$, oxidation by $\text{KMnO}_4\text{-MgSO}_4\text{-COMe}_2$, and hydrolysis by 4% NaOH-EtOH then gives (II), m.p. 137° (cf. A., 1934, 525). 3:1:5:2-OMe-C $_6\text{H}_2\text{Me}(\text{O}\cdot\text{CO}_2\text{Et})\cdot\text{COCl}$ and (I) afford similarly isosphaerophorin (III), 5:1:3:2-OH-C $_6\text{H}_2\text{Me}(\text{OMe})\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{C}_7\text{H}_{15})\cdot\text{CO}_2\text{H}$. 1:3:5:4, m.p. 137° (CH_2N_2 gives trimethylsphaerophorin). R. S. C.

Orsellinic esters. F. FUJIKAWA and H. SENGOKU (J. Pharm. Soc. Japan, 1939, 59, 91—92).—By heating lecanoric or gyrophoric acid with the requisite alcohol, *Pr* $^\alpha$, m.p. 125—126°, *Pr* $^\beta$, m.p. 115° , *Bu* $^\alpha$, m.p. 95° , *Bu* $^\beta$, m.p. 139° , isoamyl, m.p. 88° , CH_2Ph , m.p. 137—138°, and $\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, m.p. 102—103°, orsellinates are obtained. H. W.

Lichen substances. XCIII. Thamnic acid. Y. ASAHINA and M. HIRAIWA (Ber., 1939, 72, [B], 1402—1404).—Thamnic acid (I) loses CO_2 when warmed with an excess of NH_2Ph in EtOH-glycerol at 60° giving decarboxythamnolanic acid, m.p. 216° (decomp.), hydrolysed by 10% HCl in COMe_2 to decarboxythamnolic acid, new m.p. 225° , which is thus very readily obtained. The reaction is adapted to the microchemical detection of (I). Hamatommanil, m.p. 206° , is considerably more stable in presence of an excess of NH_2Ph but is partly decomposed in boiling EtOH. (I) can also be detected by means of its Ba salt. Very probably (I) is identical with hirtellic acid. H. W.

Synthesis of 6-methoxydiphenyl ether-3:4'-diacetic acid. M. TOMITA, M. SATOMI, and T. IKEDA (J. Pharm. Soc. Japan, 1938, 58, 127—130; cf. Kondo *et al.*, *ibid.*, 1933, 53, 92; A., 1932, 1048).—6-Methoxydiphenyl ether-3:4'-dicarboxyl chloride and $\text{CH}_2\text{N}_2\cdot\text{Et}_2\text{O}$ afford the 3:4'-di(diazoketone) (I), m.p. 135° , converted by $\text{Ag}_2\text{O}\cdot\text{H}_2\text{O}$ -dioxan at 60° into 6-methoxydiphenyl ether-3:4'-diacetic acid (II), m.p. 173° [diamide, m.p. 194° , obtained from (I) and aq. $\text{NH}_3\text{-AgNO}_3$ -dioxan at 60—65°, is hydrolysed

(EtOH-KOH) to (II). (I) and Ag_2O -EtOH at 60° give the Et_2 ester of (II). A. T. P.

Synthesis of methyl 3-bromohydrastate. S. UYEO and M. KATAYANAGI (J. Pharm. Soc. Japan, 1939, 59, 94-96).—7-Nitro-5:6-methylenedioxyhydrind-1-one is oxidised by 10% HNO_3 at 100° to 3-nitrohydrastic [3-nitro-4:5-methylenedioxyphthalic] acid, m.p. 236-237°, the Me_2 ester, m.p. 157-158°, of which is reduced (H_2 , PtO_2 , EtOAc) to Me_2 3-aminohydrastate, m.p. 92-93°; this is transformed (Sandmeyer) into Me_2 3-bromohydrastate, m.p. 150-151°, which readily forms Me_2 hydrastate when heated with Cu-bronze. H. W.

Chemiluminescence of hydrazides of carbonyl acids. E. S. WASSERMAN and G. P. MIK-LUCHIN (J. Gen. Chem. Russ., 1939, 9, 606-619).—Hydrazides of the types $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ ($\text{R} = \text{Ph}$, $m\text{-NO}_2\cdot\text{C}_6\text{H}_4$, $\text{CHPh}\cdot\text{CH}$), $(\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$, and $\text{R}(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ [where $\text{R} = \text{CH}_2$, $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2$, $\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})$, $\cdot\text{CH}(\text{NH}_2\cdot\text{CH}_2)\cdot$], and $[\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2]_2$ do not exhibit chemiluminescence [haematin or $\text{K}_3\text{Fe}(\text{CN})_6$ as activator], except when the radical R contains an NH_2 -group. In the series $(\text{R}\cdot\text{CO}\cdot\text{NH})_2$ luminescence exists when $\text{R} = \text{CCl}_3$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4$, or $o\text{-NH}_2\cdot\text{C}_6\text{H}_4$, but not when $\text{R} = \text{H}$ or Ph . Chemiluminescence is exhibited by $(\cdot\text{CO}\cdot\text{NH})_2$ and other cyclic hydrazides of the types $\text{R}(\cdot\text{CO}\cdot\text{NH})_2$, viz., malon-, naphthalic, 4-nitro-naphthalic, m.p. $>320^\circ$, diphenic, m.p. $>310^\circ$, o-carboxyphenylglycine, m.p. $>320^\circ$, 1-amino-2:5-diphenylpyrrole-3:4-dicarboxylic, m.p. $>320^\circ$, 4-hydroxy- and 3-nitro-phthal-, 4-sulphophthal- (N_2H_4 salt, m.p. $>310^\circ$), 3-nitro-N-phenylphthal-, and N-carbethoxymethylphthal-hydrazides.

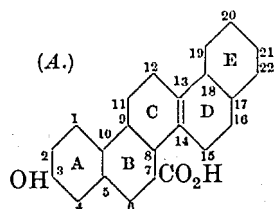
$o\text{-C}_6\text{H}_4\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$ and $o\text{-C}_6\text{H}_4\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$ do not exhibit chemiluminescence. R. T.

Bile acid, $\text{C}_{27(28)}\text{H}_{46(48)}\text{O}_6$, m.p. 252-255°, $[\alpha]_D^{25} -30.58^\circ$ in EtOH (Me ester, m.p. 94-96°), from shark bile, and keto-acid, m.p. 175°.—See A., 1939, III, 693.

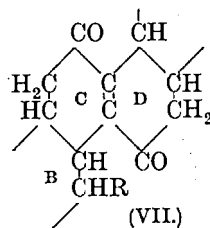
Isomerides of 3:5:6-trihydroxycholanate acid. J. HATTORI (J. Pharm. Soc. Japan, 1939, 59, 12-16).—Treatment of $\text{Me } \Delta^3\text{-3-hydroxycholenate}$ (I), m.p. 145-146°, with 40% H_2O_2 in AcOH and subsequent acetylation yields $\text{Me } \alpha\text{-5-hydroxy-3:6-diacetoxycholanate}$ (II), m.p. 150-151°, $[\alpha]_D^{25} -42.4^\circ$ in CHCl_3 [hydrolysed by alkali to $\alpha\text{-3:5:6-trihydroxycholanate acid}$, m.p. 258-259° (decomp.), $[\alpha]_D^{25} -4.37^\circ$ in EtOH [Me ester (III), m.p. 213-214°]], and $\text{Me } 3:5:6\text{-triacetoxycholanate}$ (IV), m.p. 193-193.5°, $[\alpha]_D^{25} -36.9^\circ$ in CHCl_3 , hydrolysed by alkali to 3:6-dihydroxy-5-acetoxycholanate acid, m.p. 239-240° (decomp.). This is transformed by Ag_2O and MeI into $\text{Me } 3:6\text{-dihydroxy-5-acetoxycholanate}$, m.p. 163.5-164.5°, and by $\text{MeOH-H}_2\text{SO}_4$ into $\text{Me } \beta\text{-3:5:6-trihydroxycholanate}$, m.p. 210-212°, which is acetylated to $\text{Me } 5\text{-hydroxy-3:6-diacetoxycholanate}$, m.p. 141-142.5°, $[\alpha]_D^{25} -46.9^\circ$ in CHCl_3 , hydrolysed by alkali to $\beta\text{-3:5:6-trihydroxycholanate acid}$, m.p. 236.5-237.5° (decomp.), $[\alpha]_D^{25} -3.92^\circ$ in EtOH. (II) is converted by dry HCl in Ac_2O into (IV). The production of these isomerides depends on the configuration of the two OH at C_{15} and C_{16} . Excess of BzO_2H in CHCl_3

converts (I) into $\text{Me } \alpha\text{-3-hydroxy-5:6-oxidocholanate}$ (V), m.p. 142.5-143.5°, $[\alpha]_D^{25} -52.5^\circ$ in CHCl_3 , which does not give a yellow colour with $\text{C}(\text{NO}_2)_4$ in CHCl_3 but gives a ppt. with digitonin in EtOH; it is acetylated to $\text{Me } \alpha\text{-3-acetoxy-5:6-oxidocholanate}$ (VI), m.p. 130-131°, $[\alpha]_D^{25} -47.4^\circ$ in CHCl_3 , and hydrolysed to $\alpha\text{-3-hydroxy-5:6-oxidocholanate acid}$, m.p. 210-211° (decomp.). Fission of the oxide ring of (V) by AcOH leads to (II) whereas heating with H_2O or with 50% EtOH yields (III); with HCl-MeOH it affords $\text{Me } 5\text{-chloro-3:6-dihydroxycholanate}$, m.p. 220° (decomp.), which is also obtained similarly from (II). $\text{Me } 5\text{-chloro-6-hydroxy-3-acetoxy-}$ (VII), m.p. 189-189.5°, and -3-benzoyloxy- , m.p. 186-188°, -cholanate are described. Scission of (V) with MeOH and conc. H_2SO_4 yields $\text{Me } \gamma\text{-3:5:6-trihydroxycholanate}$, m.p. 223-224° [acid, m.p. 211-212.5° (decomp.), $[\alpha]_D^{25} -12.8^\circ$ in EtOH; 3-acetate, m.p. 134-135.5°, $[\alpha]_D^{25} -40.5^\circ$ in CHCl_3]. $\text{C}_5\text{H}_5\text{N}$ and AgNO_3 transform (VII) into (VI), which is transformed by AcOH into (II). H. W.

Quinovic acid. VI. H. WIELAND, W. SCHMITT, and A. HRUBESCH [and, in part, K. KRAUS], VII. H. WIELAND and H. SCHLENK (Annalen, 1939, 539, 219-241, 242-261; cf. A., 1936, 849).—VI. Evidence is presented that quinovic acid (I) is a derivative of (A). Pyroquinovic acid (II), $[\alpha]_D^{25} -61.3^\circ$ in CHCl_3 , is obtained from (I) in 70-80% yield at 280-300°/vac. Me pyroquinovate



and MgMeI give a dimethylcarbinol (III), $\text{C}_{31}\text{H}_{52}\text{O}_2$, m.p. 187-188°, the 3-acetate (IV), m.p. 213°, of which with $\text{CrO}_3\text{-AcOH}$ at 40° yields mainly a colourless acetoxy-diketone (V), $\text{C}_{32}\text{H}_{48}\text{O}_4$ ($\text{C}\cdot\text{C}\cdot\text{CH}_2 \rightarrow \text{C}\cdot\text{C}\cdot\text{CO}$, and $\text{CMe}_2\cdot\text{OH} \rightarrow \text{COMe}$), m.p. 247°, but at 85° yields a yellow acetoxy-diketone, $\text{C}_{30}\text{H}_{44}\text{O}_4$, m.p. 267° [hydrolysed to a yellow hydroxy-diketone, $\text{C}_{28}\text{H}_{42}\text{O}_3$ (VI), m.p. 242°], with small amounts of an acid, m.p. 197°, and (V). This proves that the $\text{b-CO}_2\text{H}$ of (II) is attached to a cyclic CH. Attempts to oxidise (V) to (VI) failed. H_2O_2 , Br , N_2H_4 , and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ are without effect on (VI), which also differs from novaquinone (absorption max. at 405 and 455 $\text{m}\mu$.) in being stable to hot alkali and in having an absorption max. at 270 $\text{m}\mu$. These facts prove the presence of $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CO}$ in (VI). The yellow acid, $\text{C}_{29}\text{H}_{40}\text{O}_5$ [obtained from (II) by CrO_3 (loc. cit.) and from acetylpyroquinovic acid by oxidation, followed by hydrolysis and further oxidation], also



has $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CO}$, has an absorption max. at 268 $\text{m}\mu$., and is probably (VII) ($\text{R} = \text{CO}_2\text{H}$). Acetylpyroquinovoyl chloride (prep. by SOCl_2 at room temp.), m.p. 170° (decomp.) [with NaOH in dioxan gives the acetoxy-acid, but with boiling n-MeOH-KOH (1-2 min.) gives the hydroxy-ester], with ZnPhCl in PhMe gives the acetoxy-ketone, m.p. 161°, hydrolysed ($\text{KOH-Pr}^n\text{OH}$) to the hydroxy-ketone (VIII), $\text{C}_{35}\text{H}_{50}\text{O}_2$,

Br, $C(NO_2)_4$, etc. suggest that the ethylenic linkings may be in different places for the quinovic and pyroquinovic series. In Et_2O , (XIII) and $SOCl_2$ at 0° give *benzoylquinovoyl monochloride*, m.p. 197—198°, which with MeOH gives ? Me_1 *benzoylquinovate*, m.p. 211—212° (decomp.) [at 250° /vac. gives CO, a little CO_2 , and a (?) quinovatrienol]. When melted, (I) gives a trace of CO. Cl_2 and (I) in AcOH at room temp. give *trichloroquinovallactone* (XIV), $C_{30}H_{41}O_5Cl_3$, m.p. 287° (decomp.), $[\alpha]_D^{25} +23.1^\circ$ in $CHCl_3$ [CH_2N_2 gives a Me ester, m.p. 302° (decomp.)], and a Cl_3 -acid, $C_{30}H_{41}O_5Cl_3$, decomp. 324° (Me_2 ester, m.p. 206°); thus, (XIV) absorbs first 2 Cl, loses 1 HCl to form a monolactone, and has its $CH\cdot OH$ oxidised to CO, which then gives CCl_2 . With boiling 8% KOH-MeOH (XIV) gives KCl and <50% of a substance, $C_{30}H_{42}O_7$, m.p. 275°, in which 2 Cl are replaced by OH and one is lost as HCl giving an ethylenic linking. With boiling C_5H_5N , (XIV) loses 1 Cl as HCl, giving a substance, $C_{30}H_{40}O_5Cl_2$, m.p. 282—285°. $AgNO_3$ in C_5H_5N at room temp. replaces 1 Cl by OH, and so gives a substance, $C_{30}H_{42}O_6Cl_2$, m.p. 285°. Zn dust in AcOH gives very slowly a poor yield of a substance, m.p. 253—255° (decomp.). Me quinovate, the OH-acid, $C_{29}H_{42}O_5$, and its ester absorb no O from BzO_2H , but quinochromin absorbs 1 O. Anhydroquinovic and novic acid have $[\alpha]_D^{25} +294^\circ$ in $CHCl_3$ -EtOH (1:2) and $[\alpha]_D^{25} +123^\circ$ in $CHCl_3$, respectively. R. S. C.

Preparation of multiply unsaturated nitriles and aldehydes. II. G. WITTIG and H. HARTMANN (Ber., 1939, 72, [B], 1387—1398).—Reaction does not occur between $PhCHO$ and $CMe_2\cdot C(CN)\cdot CO_2Me$ (I) at $\sim 120^\circ$ alone or in the presence of NH_2Ac or NEt_2Ac ; NH_4OAc causes hydrolysis of (I) to $COMe_2$ and $CN\cdot CH_2\cdot CO_2Me$, which with $PhCHO$ yields $CHPh\cdot C(CN)\cdot CO_2Me$, m.p. 88—89°. In presence of piperidine and its acetate at 45° , $PhCHO$ and (I) yield Me α -cyano- δ -phenyl- β -methyl- $\Delta^{5,7}$ -pentadienate, m.p. 111.5°, in 85% yield. $CHPh\cdot CH\cdot CHO$, NH_4OAc , and (I) afford Me α -cyano- δ -phenyl- $\Delta^{5,7}$ -pentadienate, m.p. 143.5—144.5°. $CHPh\cdot CH\cdot CHO$ and Me α -cyanosorbate in presence of piperidine and AcOH give Me α -cyano- θ -phenyl- $\Delta^{5,7}$ -nonatetraenoate, m.p. 168—169°, in 25% yield. This is hydrolysed by $Ba(OH)_2$ -MeOH to the acid, m.p. 219—221°, which is decarboxylated by Cu powder at 180 — 200° to a mixture of stereoisomeric θ -phenyl- $\Delta^{5,7}$ -nonatetraenonitriles, of which a form, m.p. 146—149°, is obtained pure. Prolonged boiling of a mixture of β -ionone and $CN\cdot CH_2\cdot CO_2Me$ in AcOH containing NH_2Ac and NH_4OAc leads to Me cyano- β -ionylideneacetate, b.p. 171—172°/0.38 mm.; the non-cryst. acid is decarboxylated at 150° to β -ionylideneacetonitrile, b.p. 117—122°/1 mm., hydrolysed to β -ionylideneacetic acid, m.p. 125°. The reducibility of unsaturated nitriles $R\cdot [CH\cdot CH]_n\cdot CN$ (A) decreases rapidly with increase of n when $SnCl_4$ and HCl in Et_2O are used. $CrCl_2$ in Et_2O -HCl or dioxan-HCl at 80° , $CrBr_2$ in Et_2O -HBr, VCl_2 or $TiCl_3$ in HCl- Et_2O are ineffective but much better results are obtained with $SnBr_2$ in HBr- Et_2O or HBr-dioxan at 55 — 60° , the yield of aldehyde from (A) being 73, 65, and 50% when $n = 0, 1$, and 2, respectively. A suitable apparatus

is described. The method is not effective with $Ph\cdot [CH\cdot CH]_3\cdot CN$. H. W.

Preparation of m -dialkylaminobenzaldehydes. W. COCKER and J. O. HARRIS (J.C.S., 1939, 1092—1094).— m - $NH_2\cdot C_6H_4\cdot CH(OMe)_2$ (I) in Et_2O with 1.5N- Na_2CO_3 and Et_2SO_4 at room temp. (7 days) gives m -diethylaminobenzaldehyde, b.p. 137—138°/6—7 mm. (semicarbazone, m.p. 165°; azine, m.p. 114—115°; 2:4-dinitrophenylhydrazone, m.p. 197—198°; picrate, m.p. 145.5—146°; leuco-base, m.p. 108.5—109.5°, of the crystal-violet analogue), which gives a methiodide, m.p. 167.5—168° (decomp.), but no ethiodide. 3N- Na_2CO_3 , Pr^4I , and (I)- Et_2O , at room temp. for 21 days and then boiling for 4 days, give m -di- n -propylaminobenzaldehyde, b.p. 145—148°/5—6 mm. [semicarbazone, m.p. 172—172.5°; 2:4-dinitrophenylhydrazone, m.p. 207—208°; picrate, m.p. 136—137°; methiodide, m.p. 152°; platinichloride, m.p. 178° (decomp.)]. 1.5N- Na_2CO_3 and $CH_2\cdot CH\cdot CH_2Br$ yield m -diallylaminobenzaldehyde, b.p. 131—132°/4 mm. [semicarbazone, m.p. 133.5—134°; 2:4-dinitrophenylhydrazone, m.p. 165—165.5°; platinichloride, m.p. 161° (decomp.)], unstable in warm H_2O ; azine, m.p. 70—71°; unstable, impure picrate, m.p. 108.5—109°, which gives no methiodide. 3N- Na_2CO_3 and CH_2PhBr give m -dibenzylaminobenzaldehyde, m.p. 59—60°, b.p. 230—231°/7 mm. (semicarbazone, m.p. 185—185.5°; oxime, m.p. 125—126°; 2:4-dinitrophenylhydrazone, m.p. 230—231°; azine, m.p. 167—167.5°; impure platinichloride, m.p. 124—125°), which gives no methiodide. The order of basicity of m -dialkylaminobenzaldehydes follows no accepted rules. Steric effects may influence the results. R. S. C.

γ -Substituted resorcinol derivatives. I. Synthesis of γ -resorcaldehyde. K. NAKAZAWA (J. Pharm. Soc. Japan, 1939, 59, 57—59).—2:4:1-(OH) $_2C_6H_3\cdot CO_2H$ and $AlCl_3$ - $Zn(CN)_2$ - Et_2O , with HCl gas, give 3-aldehydo-2:4-dihydroxybenzoic acid, m.p. 195° (decomp.), converted by H_2O_2 -aq. NaOH into pyrogallol-4-carboxylic acid, m.p. 221° (decomp.), or by boiling H_2O into γ -resorcaldehyde, m.p. 154° (oxime, m.p. 167°). A. T. P.

4-Methoxy-3-chloromethylbenzaldehyde. B. REICHERT and K. AUF DEM KAMPE (Arch. Pharm., 1939, 277, 261—271; cf. A., 1937, II, 422).—4:3:1- $OMe\cdot C_6H_3(CH_2Cl)\cdot CHO$ (I) with $MeNO_2$ ($EtOH\cdot KOH$) and $EtNO_2$ ($EtNH_2$) yields respectively β -nitro- α -(4-methoxy-3-chloromethylphenyl)-ethylene, m.p. 118°, and -propylene, m.p. 80°. Hydrolysis (dil. H_2SO_4) of (I) gives $OMe\cdot C_6H_3(CH_2\cdot OH)\cdot CHO$ (II) in 78% yield. (II) similarly yields β -nitro- α -(4-methoxy-3-hydroxymethylphenyl)-ethylene, m.p. 104—105° (acetate, m.p. 131—132°), and -propylene, m.p. 90°; reduction (H_2 , Pd-C, C_5H_5N at 55°) of the former affords 4-methoxy-3-hydroxymethylphenyl-acetaldoxime, m.p. 119—120°, further reduced (H_2 , PtO $_2$, $EtOH\cdot H_2C_2O_4$ or Na-Hg + $EtOH\cdot AcOH$) to the ethylamine (H oxalate, m.p. 147—148°). (II) with $CH_2(CO_2H)_2$, C_5H_5N , and a trace of piperidine yields 4-methoxy-3-hydroxymethylcinnamic acid, m.p. 190—191°, reduced (H_2 , Pd-C, 80% MeOH at 35°) to β -6-methoxy-m-tolylpropionic acid, m.p. 98—99° [Me ester (CH_2N_2), m.p. 45°]. Oxidation of (I) or (II) with dil. HNO_3 or of (II) with CrO_3 yields 4-methoxyisophthalaldehyde,

m.p. 123—124° (dioxime, m.p. 170—172°), further oxidised (KMnO₄) to 4:3:1-OMe-C₆H₃(CO₂H)₂.

A. LI.

2:4-Dinitrophenylhydrazones, m.p. 198°, of *p*-hydroxyphenylpyruvic acid.—See A., 1939, III, 725.

Synthesis of substituted alicyclic methyl ketones. II. Hydroxymethyl ketones. W. A. YARNALL and E. S. WALLIS (J. Org. Chem., 1939, 4, 284—288).—Attempts to condense cyclohexanone (I) with CH₂Cl·CHCl·CO₂Et in presence of NaOEt leads under all conditions to CH₂·CHCl·CO₂Et. (I) does not condense with OH·CH₂·CHCl·CO₂Et. CH₂Cl·CHCl·CO₂H is obtained in 18% yield by addition of Cl₂ to CH₂·CH·CH₂·OH and oxidation of the dichlorohydrin by HNO₃, or in 85% yield by passage of Cl₂ through CH₂·CH·CHO at <−5° and treatment of the product with a mixture of conc. and fuming HNO₃ at 40—50°. Gradual addition of Mg cyclohexyl chloride to a suspension of CN·CH₂·OMgI (obtained from OH·CH₂·CN and MgMeI) in Et₂O gives cyclohexyl CH₂·OH ketone, isolated as the 3:5-dinitrobenzoate, m.p. 110—111°. The 3:5-dinitrobenzoates of cyclopentyl and 2-methylcyclopentyl CH₂·OH ketones have m.p. 100° and 103°, respectively. 2-Methylcyclopentanone is reduced to the alcohol, which is converted in the usual manner into 2-methylcyclopentyl chloride, b.p. 122—124°/atm. pressure (some decomp.). H. W.

Hydrogen fluoride as a condensing agent. VII. Acylation of aromatic compounds. J. H. SIMONS, D. I. RANDALL, and S. ARCHER. VIII. Alkylation of benzene by esters. J. H. SIMONS, S. ARCHER, and D. I. RANDALL (J. Amer. Chem. Soc., 1939, 61, 1795—1796, 1821—1822; cf. A., 1939, II, 362).—VII. In HF at 80—100° PhMe with AcOH, Ac₂O, or AcCl gives *p*-C₆H₄Me·COMe, with BzOH or BzCl gives *p*-C₆H₄Me·COPh, and with Bu^oCO₂H gives *p*-C₆H₄Me·COBu^o; PhOH and AcOH give *p*-OH·C₆H₄·COMe; C₆H₆ and AcCl give C₆H₅Me.

VIII. With HF in an excess of C₆H₆ at 80—100°, Bu^oOAc gives PhBu^o and C₆H₅Me; Pr^oOAc gives PhPr^o, C₆H₅Me, and *p*-C₆H₄Pr^o·COMe; Bu^oOAc or sec-BuO·COPr^o gives PhBu^o-sec.; CH₂Ph·OAc gives CH₂Ph₂. The reaction mechanism is discussed.

R. S. C.

Action of mixed organo-magnesium compounds on osazones. P. GRAMMATICAKIS (Compt. rend., 1939, 208, 1998—2000; cf. A., 1937, II, 248, 287).—COPh·CH·N·OH (1 mol.) with NHPH₂·HCl (2:2 mols.) in warm EtOH gives phenylglyoxalphenylosazone (I) (100%), which with MgPhBr in Et₂O gives *ω*-phenylhydrazino-*ω*-phenylacetophenonephenylhydrazones (II), m.p. 124°, and a small amount of (CPh·N·NHPH₂)₂ (III). (I) with MgEtBr affords *ω*-phenylhydrazino-*ω*-ethylacetophenonephenylhydrazones, m.p. 123°. Glyoxalphenylosazone with MgPhBr similarly affords (II), (III), (I), and CHPh·N·NHPH. (I) does not react with MgMeI in Et₂O. (III) in boiling Et₂O/14 hr. with a large excess of MgMeI, MgEtBr, or MgPhBr forms no additive products. Cinnamaldehydephenylhydrazones with MgEtBr similarly affords *α*-phenylhydrazino-*α*-styrylpropane, b.p. 185—187°/1 mm. J. L. D.

Heterocyclic compounds containing nitrogen. XLIV. 2:2'-Dinitrodeoxybenzoin. P. RUGGLI and A. DINGER (Helv. Chim. Acta, 1939, 22, 908—911).—The product of the oxidation of *o*-NO₂·C₆H₄·CH₂·CO·CO₂H by CaOCl₂ is shown to be 2:2'-dinitrodeoxybenzoin, m.p. 166° (lit. 160°). Hydrogenation (Raney Ni in EtOH-EtOAc-H₂O) of it yields 2-*o*-aminophenylindole, m.p. 153° (Ac derivative, m.p. 151—152°), and *α*β-2:2'-diaminodiphenylethane, m.p. 67° (Ac₂ derivative, m.p. 250°). H. W.

Influence of route chosen for an asymmetric synthesis on the configuration of the resulting enantiomorph. S. M. PARTRIDGE (J.C.S., 1939, 1201).—The formation of (+)- and (−)-OH·CPhEt·COPh from (−)-OH·CHPh·CO₂H (Roger, A., 1939, II, 111) and of (+)- and (−)-OMe·C₆H₄·CMe(OH)·CO₂H (McKenzie *et al.*, A., 1932, 1037) is determined by the order in which the substituents are introduced and thus contradicts the conclusions of Roger. R. S. C.

Rearrangement of *α*-hydroxy-carbonyl compounds. P. G. STEVENS (J. Amer. Chem. Soc., 1939, 61, 1714—1716).—Isomerism, CH₂Ar·CO·CHAr'·OH ↔ CH₂Ar·CH(OH)·COAr', is demonstrated, thus supporting Hibbert's theory of lignin formation. *α*-Hydroxy-*β*-keto-*γ*-phenyl-*α*-*p*-chlorophenylpropane (I), m.p. 125.5—126°, is prepared from *p*-C₆H₄Cl·CO·CH(OH)·CHPh·CO₂H and from *p*-C₆H₄Cl·CH(OH)·CN + CH₂Ph·MgCl. *β*-Hydroxy-*α*-keto-*γ*-phenyl-*α*-*p*-chlorophenylpropane (II), m.p. 43—44°, is converted into (I) by Na₂CO₃ in hot 95% EtOH; the reverse transformation was effected in poor yield under narrow conditions. With strong alkali, (I) gives *p*-C₆H₄Cl·CO₂H and *α*-hydroxy-*β*-phenyl-*α*-*p*-chlorophenylpropionic acid (III), m.p. 201—202°, the reaction mechanism being: (I) or (II) ↔ CH₂Ph·C(OH)·C(OH)·C₆H₄Cl → CH₂Ph·CO·CO·C₆H₄Cl (IV) + CH₂Ph·CH₂·CO·C₆H₄Cl (not isolated); (IV) gives (III) by benzylic acid rearrangement or C₆H₄Cl·CO₂H by cleavage. The structure of (III) is proved by synthesis from *β*-*p*-chlorobenzoyl-*α*-phenylethylene oxide by alkali and by oxidation to *p*-chlorodeoxybenzoin, m.p. 104.5—105.2°. H₂-PtO₂ in MeOH reduces *p*-C₆H₄Cl·CO·CH·CHPh to *p*-C₆H₄Cl *β*-phenylethyl ketone, m.p. 75—76°, converted by Br·CHCl₃ into *p*-C₆H₄Cl *α*-bromo-*β*-phenylethyl ketone, m.p. 92—93°, which with Na₂CO₃ in aq. EtOH gives (II). R. S. C.

Functional aptitude of the methyl group. II. Derivatives of benzophenone and benzil. L. CHARDONNENS and J. VENETZ (Helv. Chim. Acta, 1939, 22, 822—836).—Me in substituted benzophenones is activated if Bz is in the *para*- and NO₂ in the *ortho*-position but not if the placing of the substituents is reversed. 3-Nitro-4-methylbenzophenone (I) condenses with *p*-NMe₂·C₆H₄·CHO in presence of piperidine at 155—160° to 3-nitro-4-*p*-dimethylaminostyrylbenzophenone, m.p. 180°. 3-Nitro-4-*p*-methoxystyrylbenzophenone, m.p. 156°, is obtained similarly. PhCHO and the requisite benzophenone afford 3:3'-dinitro-, m.p. 155—156°, 3:5-dinitro-, m.p. 129.5—130.5°, and 3:5:3'-trinitro-, m.p. 164.5°, -4-styrylbenzophenone. 3:3'-Dinitro-4-methylbenzophenone

and *p*-NO-C₆H₄-NMe₂ in boiling EtOH containing anhyd. Na₂CO₃ slowly afford 2-nitro-4-*m*'-nitrobenzoylbenzald-*p*'-dimethylaminoanil, m.p. 147—148°, and 2-nitro-4-*m*'-nitrobenzoylbenzaldoxime N-*p*-dimethylaminophenyl ether, m.p. 234°. *p*-NO-C₆H₄-NMe₂ and (I) yield 2-nitro-4-benzoylbenzald-*p*-dimethylaminoanil, m.p. 174—175°, and the corresponding nitro-*ne*, m.p. 217°. 3:5-Dinitro-4-methylbenzophenone appears to give exclusively 2:6-dinitro-4-benzoylbenzald-*p*-dimethylaminoanil, m.p. 157—158°. 5:2-NO₂-C₆H₃Me·CO₂H is transformed by the successive actions of SOCl₂ and C₆H₅-AlCl₃ into 5-nitro-2-methylbenzophenone, m.p. 79°, which is transformed by *p*-NO-C₆H₄-NMe₂ into 4-nitro-2-benzoylbenzaldoxime N-*p*-dimethylaminophenyl ether, m.p. 240°. 3:5:2-(NO₂)₂-C₆H₂Me·CO₂H is transformed into 3:5-dinitro-2-methylbenzophenone, m.p. 88°, which yields 3:5-dinitro-2-styrylbenzophenone, m.p. 119—120°, with PhCHO and piperidine at 130°, and 2:4-dinitro-6-benzoylbenzald-*p*-dimethylaminoanil, m.p. 190—192°, with *p*-NO-C₆H₄-NMe₂ in boiling EtOH containing Na₂CO₃. 3:3'-Dinitro-4:4'-dimethylbenzophenone and PhCHO afford 3:3'-dinitro-4:4'-distyrylbenzophenone, m.p. 202—203°, whilst 3:3'-dinitro-4:4'-diformylbenzophenone di-*p*-dimethylaminoanil, m.p. 200—201°, is obtained from *p*-NO-C₆H₄-NMe₂. 3:3'-Dinitro-4:4'-dimethylbenzil [quinoxaline, m.p. 179—180°, from *o*-C₆H₄(NH₂)₂] affords 3:3'-dinitro-4:4'-distyrylbenzil, m.p. 224° or 196—197° (quinoxaline, m.p. 207—208°). H. W.

Mechanism of reduction of conjugated systems with terminal carbonyl groups. Dienols obtained from unsaturated αδ-diketones. R. E. LUTZ and W. G. REVELEY (J. Amer. Chem. Soc., 1939, 61, 1854—1859).—Reduction of COR·CH:CH·COR (I) catalytically or by metal is shown to occur by 1:6-addition, giving OH·CR:CH·CH:CR·OH (II) as primary product. When (I) (R = mesityl) is hydrogenated (Pt) in EtOH at 0° and the solution is filtered under N₂ and run into aq. or EtOH-I, the amount of (II) (R = mesityl) present is determined by the I consumed [(II) + 2I → (I)]; this amount depends on the time of manipulation and with short times rises to 93.7%; if the solution is kept, preferably after addition of a little piperidine as catalyst, ketonisation gives nearly 100% yields of (2:4:6-C₆H₃Me₃·CO·CH₂)₂ (III). The amount of (II) formed was checked (concordant results) by converting the (II) by NaHSO₃ in boiling 60% EtOH into the H₂O-sol. Na αδ-diketo-αδ-dimesitylbutane-β-sulphonate (Pb salt) and weighing the insol. (III). Zn dust in 1:1 AcOH-Et₂O at -5° to 0° gives a solution containing (I method) 61% of (II). Ketonisation of (II) (R = mesityl) in EtOH is very slow at 0°, but rises with increasing temp.; at 26—29° the half-life period is ~12 hr. at rest, but if the solution is disturbed, ketonisation is much more rapid. (II) (R = mesityl) could not be isolated. The amount of (II) (R = mesityl) obtained by hydrogenation at 0° was in 95% EtOH 91—94, dioxan-EtOH (4:1) 90, EtOAc 78, Pr²O 60, C₆H₆ (at 5°) 54, *n*-C₆H₁₄ 60, decahydronaphthalene 17, and AcOH-EtCO₂H (63:37) ~40—50%. The dimagnesium enolate of (III) [prep. by heating with MgPhBr

(excess) in diisoamyl ether at 110°] with I in 95% EtOH at 0° gives an excellent yield of *trans*-(I) (R = mesityl). OMgBr·CPh:CH·CPh:OMgBr [prep. from (CHBz)₂ by MgPhBr] with I-EtOH gives CHBz:CPhBz (no CH₂Bz·CHPhBz) and 2:3:4:5-tetraphenylfuran (formed from the CHBz:CPhBz by the unused MgPhBr); this confirms the author's mechanism for addition of MgRHal to (I). Isolation of OH·CR:CH·CR:CR·OH (R = mesityl), m.p. 70—71°, and of four stable mono-enols, OH·CR:CR·CHR·COR, is announced without details. R. S. C.

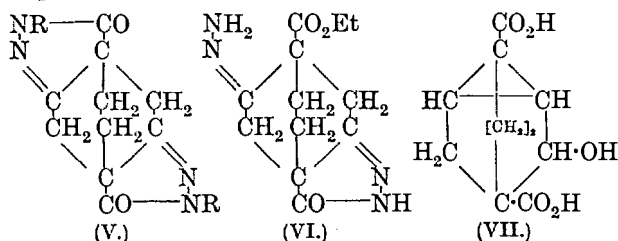
Synthesis of benzil-*o*-carboxylic and β-deoxybenzoin-*o*-carboxylic acids. B. Hof (Compt. rend., 1939, 208, 2082—2084).—Phthalonic anhydride, C₆H₆, and AlCl₃ at 80° afford a mixture of the yellow, m.p. 141.5°, and colourless, m.p. 125°, forms of benzil-*o*-carboxylic acid. PhMe similarly affords 4'-methylbenzil-2-carboxylic acid and a colourless form, m.p. 146°. Homophthalic anhydride similarly gives (30—85%) *p*-tolyl, new m.p. 160°, *p*-anisyl, m.p. 150°, 3:4-dimethoxyphenyl, m.p. 185°, and 4-hydroxy-2-methyl-5-isopropylphenyl *o*-carboxybenzil ketone, m.p. 184°. J. L. D.

Refractive indices and molecular refractivities of 3-methylcyclohexanone and pulegone.—See A., 1939, 1, 405.

Hydroaromatic series. VI. Addition of 6-methoxy-1-vinyl-3:4-dihydronaphthalene to Δ¹-cyclopentenone and 4:4-dibromo-Δ¹-cyclopentene-3:5-dione. E. DANE and K. EDER (Annalen, 1939, 539, 207—212; cf. A., 1939, II, 318).—Δ²-cyclopentenyl acetate, b.p. 58—61°/20 mm., is best obtained, with some 1:2-diacetoxycyclopentane, b.p. 115—118°/20 mm., from cyclopentene by Pb(OAc)₄ in AcOH at 50°. Δ²-cyclopentenol, b.p. 68—70°/40 mm., obtained therefrom, is oxidised by CrO₃ in dil. H₂SO₄ to Δ²-cyclopentenone, b.p. 42°/10 mm. (2:4-dinitrophenylhydrazones, m.p. 165°). With butadiene in dioxan at 120—160°, this gives 4:7:8:9-tetrahydroindan-1-one, an oil (dinitrophenylhydrazones, m.p. 199°), and with 6-methoxy-1-vinyl-3:4-dihydronaphthalene (I) gives 1'-keto-7-methoxy-1:2:3:9:10:11-hexahydrocyclopentano-3':2'- or 2':3'-1:2-phenanthrene, m.p. 141° (dinitrophenylhydrazones; HBr-AcOH gives a cryst. phenol, dehydrated by benzoquinone to a cryst. compound). 4:4-Dibromo-Δ¹-cyclopentene-3:5-dione with butadiene or (I) in dioxan at 110—115° gives 2:2-dibromo-4:7:8:9-tetrahydroindane-1:3-dione, m.p. 92°, and 4':4'-dibromo-3':5'-diketo-7-methoxy-1:2:3:9:10:11-hexahydrocyclopentano-1':2'-1:2-phenanthrene, m.p. 166°, respectively. R. S. C.

para-Bridge formation with ethyl succinylsuccinate. I. Formation of dicyclo-[1:2:2]-heptane, dicyclo-[2:2:2]-octane, and dicyclo-[3:2:2]-nonane systems. P. C. GUHA (Ber., 1939, 72, [B], 1359—1373; cf. A., 1936, 1252).—The action of CH₂I₂, I, or Br on Et₂ sodiosuccinosuccinate (I) gives Et₂ 2:5-dihydroxyterephthalate (II), m.p. 133° (Ac derivative, m.p. 154°), identified by conversion by dil. HCl at 180° into quinol. CH₂Br₂ and (I) give a very small yield of Et₂ dicyclo-[1:2:2]-heptane-2:5-dione-1:4-dicarboxylate, b.p. 110°/1 mm. COBr₂

and (I) in C_6H_6 appeared to afford an *isomeride*, m.p. 132° , of (I) which gives a pale red colour with $FeCl_3$ in EtOH. $CHBr(CO_2Et)_2$ and (I) yield a product, m.p. $127-128^\circ$, which gives a blue-green colour with $FeCl_3$ and is not identical with (I) or (II). $(CH_2Br)_2$ and (I) give Et_2 dicyclo-[2:2:2]-octane-2:5-dione-1:4-dicarboxylate (III), m.p. 112° (*disemicarbazone*, m.p. $263-264^\circ$), which when heated with H_2O containing a few drops of HCl at 200° , or boiled with 50% H_2SO_4 or 18% HCl until a clear solution is obtained, is hydrolysed to the dicarboxylic acid (IV), m.p. 286° (*disemicarbazone*, m.p. 257°). This is partly decarboxylated at $270-280^\circ$ /vac. to dicyclo-[2:2:2]-octane-2:5-dione-1:4-dicarboxylic acid, m.p. $216-217^\circ$. (IV) is readily re-converted into (III) by EtOH-HCl, which gives a *dioxime*, m.p. 210° , *mono-oxime*, m.p. 167° , is transformed by $NHPh \cdot NH_2$ into the



pyrazolone compound [(V), R = Ph], m.p. $188-189^\circ$, by boiling NH_2Ph into the *dianilide*, m.p. 193° , and by $N_2H_4 \cdot H_2O$ in EtOH into the *dipyrazolone* derivative [(V), R = H], m.p. 326° , and the *monopyrazolone* compound (VI), m.p. 204° , characterised by the formation of a *CHPh* derivative, m.p. 281° . Boiling 10% KOH-EtOH transforms (III) into $\beta\beta'$ -dicarboxysuberic acid, m.p. $177-178^\circ$, which gives a mixture when esterified in the usual manner. Oxidation of (III) with $KMnO_4$ yields $(\cdot CH_2 \cdot CO_2H)_2$, $H_2C_2O_4$, and an acid, m.p. 150° , which is not adipic acid; fuming HNO_3 gives $H_2C_2O_4$ and a trace of $(\cdot CH_2 \cdot CO_2H)_2$. (III) is largely unchanged by Na and EtOH under CO_2 . Reduction with Na-Hg in EtOH-AcOH leads to Et_2 dicyclo-[2:2:2]-octane-2:5-diol-1:4-dicarboxylate, b.p. $200-204^\circ/3$ mm.; with H_2 -PtO₂ activated by $FeCl_3$ in AcOH at $25^\circ/2.5$ atm. to the isomeric *diol diester*, b.p. $196-197^\circ/5$ mm., and by Zn-Hg and boiling dil. HCl to dicyclo-[2:2:2]-octane-1:4-dicarboxylic acid, m.p. 385° (Et_2 ester, b.p. $140-145^\circ/3$ mm.), and the acid (VII), m.p. 315° (Et_2 ester, b.p. $180-190^\circ/4$ mm.). Dry (I) and $Br \cdot [CH_2]_3 \cdot Br$ at $170-175^\circ$ give Et_2 dicyclo-[2:2:3]-nonane-2:5-dione-1:4-dicarboxylate (VIII), m.p. 132° (*disemicarbazone*, m.p. 227°), and a viscous yellow liquid, b.p. $180-190^\circ/5$ mm., which does not react with $FeCl_3$ and does not give a semicarbazone. Acid hydrolysis of (VIII) gives the dicarboxylic acid, m.p. 238° (*disemicarbazone*, m.p. 217°), readily re-esterified to (VIII). (VIII) and $NHPh \cdot NH_2$ give a *dipyrazolone* compound [cf. (V), R = Ph; $[CH_2]_3$ instead of $[CH_2]_2$], m.p. $231-232^\circ$, and with $N_2H_4 \cdot H_2O$ a *substance* [cf. (V), R = H; $[CH_2]_3$ instead of $[CH_2]_2$], m.p. 321° . By the hydrolysis of (VIII) with 5% KOH-EtOH three CO-dicarboxylic acids, $C_{10}H_{14}O_5$, of the cycloheptane series are obtained with m.p. 163° , 181° (*semicarbazone*, m.p. 220°), and 199° [Et ester, b.p. $195-205^\circ/3$ mm. (*semicarbazone*,

m.p. 152°)], respectively. (VIII) is largely unchanged by Na-Hg in EtOH-AcOH but is reduced (Clemmensen) to dicyclo-[2:2:3]-nonane-1:4-dicarboxylic acid, m.p. $>360^\circ$. H. W.

para-Bridge formation with ethyl succinotetracarboxylate. II. Synthesis of dicarbethoxy-suberic ester and its cyclisation to dicyclo-[2:2:2]-octanedione by double Dieckmann condensation. P. C. GUHA and C. KRISHNAMURTHY (Ber., 1939, 72, [B], 1374-1379).— $Et_2 \beta\beta\beta'\beta'$ -tetracarboxysuberate, m.p. 69° , is obtained from $(CH_2Br)_2$ and Et_2 sodiocarbethoxysuccinate or from $CH_2Br \cdot CO_2Et$ and Et_2 disodiobutane- $\alpha\delta\delta$ -tetracarboxylate. It is slowly hydrolysed by boiling HCl (1:1) to $\beta\beta'$ -dicarboxysuberic acid, m.p. $177-178^\circ$ [Et_4 ester (I), b.p. $205^\circ/2$ mm.]. Gradual addition of (I) to mol. Na suspended in C_6H_6 at room temp. gives unidentified alkali-insol. material which yields a *semicarbazone*, m.p. $240-242^\circ$ (decomp.), and a portion sol. in alkali which is hydrolysed and decarboxylated by HCl (1:1) to dicyclo-[2:2:2]-octane-2:5-dione, m.p. $205-206^\circ$ (*disemicarbazone*, m.p. $244-245^\circ$). H. W.

para-Bridge formation with ethyl succinotetracarboxylate. III. Resolution of dicyclo-[2:2:2]-octane-2:5-dione-1:4-dicarboxylic acid into its optical antipodes. P. C. GUHA and S. K. RANGANATHAN (Ber., 1939, 72, [B], 1379-1380).—Crystallisation of the brucine salt of the *dl*-acid from boiling H_2O gives the normal *brucine* salt (I) ($+3H_2O$), $[\alpha]_D^{25} = -70.87^\circ$ in H_2O , of *d*-dicyclo-[2:2:2]-octane-2:5-dione-1:4-dicarboxylic acid, m.p. 271° , $[\alpha]_D^{25} +23.85^\circ$ in H_2O . Conc. of the mother-liquors from (I) with periodical removal of the salt which separates leaves a salt from which the *l*-acid, $[\alpha]_D^{25} -23.24^\circ$ in H_2O , is isolated. H. W.

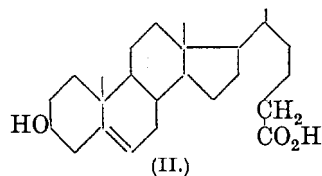
Synthesis of substituted alicyclic methyl ketones. I. W. A. YARNALL and E. S. WALLIS (J. Org. Chem., 1939, 4, 270-283; cf. A., 1937, II, 294).—Addition of powdered NaOEt to cyclohexanone and $CHMeCl \cdot CO_2Et$ affords $Et \alpha:1$ -oxido- α -cyclohexylpropionate, b.p. $126-128^\circ/19$ mm., in 54% yield; the usual brown colour is avoided if the mixture is cooled to -80° and the yield is increased to 68%. In presence of Et_2O , anhyd. C_6H_6 , or C_6H_6 + light petroleum the yields are 34, 47, and 54%, respectively. The use of an excess of α -halogeno-ester and condensing agent is advantageous, and $CHMeCl \cdot CO_2Et$ is superior to $CHMeBr \cdot CO_2Et$. $Et \alpha:1$ -oxido- α -cyclopentylpropionate, b.p. $128^\circ/25$ mm., is prepared in poorer yield from cyclopentanone. Excellent yields of the glycidic acids are obtained by hydrolysis of the esters with NaOH-EtOH, the Na salt being sometimes allowed to crystallise; when the acids are kept in solution before isolation small amounts of ketones are frequently formed. Pyrolysis of the acids at ordinary or reduced pressure gives low yields of ketones and appreciable amounts of resinous material. Attempts to obtain cyclohexyl Me ketone (I) from $Et \alpha$ -hydroxy- α -1-chlorocyclohexylpropionate by rearrangement under the influence of alkali show that the rate of re-formation of glycidic ester exceeds that of hydrolysis so that only traces of ketone are produced. $\alpha:1$ -Oxido- α -cyclohexylprop-

ionic acid and HCl yield α -hydroxy- α -1-chlorocyclohexylpropionic acid, which when dissolved in aq. Na_2CO_3 and steam-distilled gives (I) in 29% yield and a mixture of acids which yields some (I) when pyrolysed. Much better results are secured by boiling the acid in $\text{C}_5\text{H}_5\text{N}$, whereby 75% yields of (I) are obtained but only 25% yields of cyclopentyl Me ketone. Alternatively the glycidic acids are transformed into their Na salts, which are heated with an equiv. proportion of NaOH, thus giving 45–56% of ketone. By use of a large excess of $\text{CHMeCl}\cdot\text{CO}_2\text{Et}$ and NaOEt and prolonged boiling of the Et_2O solution, dehydroandrosterone (II) is almost completely converted into the non-cryst. glycidic ester, which is hydrolysed to a mixture from which acids, m.p. 183–185° and 240–244°, are isolated. The crude condensation mixture is dissolved in Et_2O and thoroughly washed; any propionates are removed at 50–70°/high vac. and unchanged (II) as its semicarbazone. The residual mixture of glycidic ester and androstenediol is hydrolysed by NaOH–EtOH and small amounts of Δ^5 -pregnenolone (III) and Δ^5 -isopregnenolone are isolated as their semicarbazones, which are hydrolysed to the free ketones (separable by digitonin). Most attempts to improve the yield of (III) failed owing to the stability of the glycidic acid. Better results are, however, obtained when the acid is treated with HCl in dry Et_2O and the product is boiled in $\text{C}_5\text{H}_5\text{N}$; the ketones are isolated as their semicarbazones, which are hydrolysed to a cryst. product, m.p. 110–114°. This is brominated, oxidised, and debrominated to progesterone, identical with that obtained from stigmastrol. The possible formation of Δ^4 -pregnenolone is mentioned.

H. W.

Δ^5 -Norcholesten-3-ol-25-one, an oxidation product of cholesteryl acetate dibromide. J. HATTORI (J. Pharm. Soc. Japan, 1938, 58, 150–153). — Δ^5 -Norcholesten-3-ol-25-one (I), m.p. 126–127° (sinters at 117°) [acetate, m.p. 139–140° (semicarbazone, decomp. 233–234°; oxime, m.p. 182°; dibromide, decomp. 125–126°); mono-oxime, m.p. 176–177°; monodinitrophenylhydrazone, m.p. 159–160°; dibromide, decomp. 130–131°], is isolated from the oxidation products of cholesteryl acetate dibromide by a method similar to that of Ruzicka *et al.* (A., 1937, II, 506). 3-Acetoxy- Δ^5 -cholenic acid, m.p. 189° (corr.), and SOCl_2 give the chloride, converted by CH_2N_2 into the corresponding diazo-

ketone, decomp. 158°. The latter and $\text{NH}_3\cdot\text{AgNO}_3\text{--EtOH}$ afford 3-acetoxy- Δ^5 -homocholenamide, m.p. 200–204° (corr.), and thence 3-hydroxy- Δ^5 -homocholenic acid (II), decomp. 217–



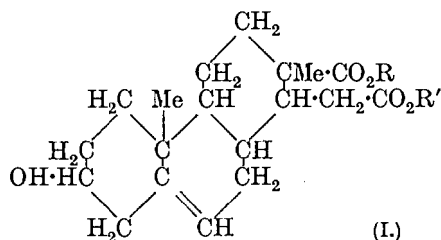
(II.)

219° (corr.) (sinters at 210°) (*Et* ester). The acetate, m.p. 188–191° (corr.), of (II) then gives, through the chloride and diazoketone (by $\text{HCl--Et}_2\text{O}$), the corresponding CH_2Cl ketone, m.p. 182–184°, converted by Zn--AcOH into the acetate, m.p. 137.5–138.5° (corr.), of (I).

A. T. P.

trans-Androsterone Me ether, m.p. 91°.—See B., 1939, 885.

Sterols. XVI. Monoalkyl 3-hydroxy- $\Delta^{5:6}$ - α -tiobilienates. XVII. Synthesis of *trans*-dehydroandrosterone. S. KUWADA and K. NAKAMURA (J. Pharm. Soc. Japan, 1938, 58, 254–256, 257–259).—XVI. Hydrolysis of Me_2 3-hydroxy- $\Delta^{5:6}$ - α -tiobilienate, m.p. 112°, for a short time with 0.2N-KOH–EtOH gives the *Me*₁ ester (I) ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$), m.p. 214.5–216.5°, $[\alpha]_D^{25} -75^\circ$ [acetate (II), m.p. 168.5–169.5°]; prolonged treatment gives the *Et* ester (I) ($\text{R} = \text{Et}$, $\text{R}' = \text{H}$), m.p. 176–177° (uncorr.), $[\alpha]_D^{25} -75.4^\circ$ to -76.4° [acetate, m.p. 137.5–139°], previously believed to be a *Me* ester. 3-Hydroxy- $\Delta^{5:6}$ - α -tiobilienic acid with $\text{MeOH--H}_2\text{SO}_4$ gives the *Me* ester [(I), $\text{R} = \text{H}$, $\text{R}' = \text{Me}$], m.p. 186.5–188°, $[\alpha]_D^{25} -55.9^\circ$, and with CHMeN_2 gives



(I.)

the *Et*₂ ester, m.p. 103.5–104.5°, hydrolysed by 0.2N-KOH–EtOH to (I) ($\text{R} = \text{Et}$, $\text{R}' = \text{H}$), the identity of which with the previous prep. is proved by crystallographic and X-ray data.

XV. The acid chloride from (II) (prep. by SOCl_2) and $\text{CH}_2\text{N}_2\text{--Et}_2\text{O}$ give the oily diazo-ketone, which with $\text{NH}_3\text{--AgNO}_3$ in EtOH yields β -*Me* 3-acetoxy- $\Delta^{5:6}$ - α -homotiobilien- α -amide (III), m.p. 165–166°. $\text{H}_2\text{SO}_4\text{--EtOH}$, followed by 0.2N-KOH–EtOH, then gives β -*Me* 3-hydroxy- $\Delta^{5:6}$ - α -homotiobilienate, m.p. 211–212°, hydrolysed by 15% KOH

at 150° to 3-hydroxy- $\Delta^{5:6}$ - α -homotiobilienic acid (IV), decomp. 248–248.5°, which is also obtained directly from (III) by 30% KOH at 100° or 15% KOH at 150–160°. Boiling 10% KOH–EtOH converts (III) into 3-hydroxy- $\Delta^{5:6}$ - α -homotiobilienamide, decomp. 255–256°, hydrolysed to (IV) by $\text{H}_2\text{SO}_4\text{--EtOH}$. When the anhydride (prep. by Ac_2O) of (IV) is first heated at 250°/vac. for 10–15 min. and then distilled at 250–260°/high vac., it gives *trans*-dehydroandrosterone acetate. M.p. etc. are corr.

R. S. C.

Steroids. XXII. 17-Epimeric methylandrostenediols and methyltestosterone. K. MIESCHER and W. KLARER (Helv. Chim. Acta, 1939, 22, 962–969).—The mother-liquors obtained in the prep. of 17-methylandrostenediol (I) by the action of MgMeI on *t*-dehydroandrosterone, after removal of unchanged ketone by $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, afford 17-isomethylandrostenediol [17-methyl- Δ^5 -androstene-3 β :17 α -diol] (II), m.p. 203–204°, $[\alpha]_D^{25} -81^\circ$ in EtOH, -84.5° in CHCl_3 . (II) gives a 3-monoacetate, m.p. 160–161°, $[\alpha]_D^{25} -77^\circ$ in EtOH, but does not yield a diacetate, whereas (I) is converted by boiling Ac_2O into 17-methyl- Δ^5 -androstene-3 β :17 α -diol diacetate, m.p. 145–146°, $[\alpha]_D^{25} -59^\circ$ in EtOH. $\text{Al}(\text{OPr}^i)_3$ converts (II) in boiling $\text{PhMe--cyclohexanone}$ into 17-isomethyl-

testosterone [17-methyl- Δ^4 -androst-17c-ol-3-one] (III), m.p. 182—183°, $[\alpha]_D^{25} +66^\circ$ in EtOH, $+72^\circ$ in CHCl_3 [semicarbazone, m.p. 220—222° (decomp.); 17-methyltestosterone semicarbazone has m.p. 226° (decomp.) or m.p. 270—272° (decomp.) in sealed tube]. 17-Methyltestosterone (IV) is transformed by Ac_2O - $\text{C}_5\text{H}_5\text{N}$ at 130—140° into its acetate, m.p. 176—176.5°, $[\alpha]_D^{25} +69^\circ$ in EtOH, whereas (III) gives resins in these circumstances and is unattacked under milder conditions. Distillation of (IV) with anhyd. CuSO_4 at 135—150°/0.01 mm. yields the ketone, $\text{C}_{20}\text{H}_{28}\text{O}$, m.p. 135—136°, $[\alpha]_D^{25} +137^\circ$ in EtOH [semicarbazone, m.p. 230° (decomp.)], also obtained from (III). This is oxidised by OsO_4 to the ketodiol, $\text{C}_{20}\text{H}_{30}\text{O}_3$, m.p. 238°, $[\alpha]_D^{25} +51^\circ$ in EtOH. H. W.

Steroids. XXI. $\alpha\beta$ -Unsaturated aldehydes of the pregnene series. K. MIESCHER, A. WETTSTEIN, and C. SCHOLZ (Helv. Chim. Acta, 1939, 22, 894—907).— $\Delta^{4:13:17:20}$ -Pregnadien-21-ol-3-one in C_6H_6 is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ -aq. H_2SO_4 and then treated with $(\text{CH}_2\text{CO})_2\text{O}$ in $\text{C}_5\text{H}_5\text{N}$, thus giving $\Delta^{4:5:17:20}$ -pregnadien-3-one-21-al (I), m.p. 149—152°, $[\alpha]_D^{25} +139^\circ$ in abs. EtOH. The mixture of diols obtained from 17-allyltestosterone and OsO_4 is oxidised by KIO_4 and aq. H_2SO_4 at room temp. to $\Delta^{4:5}$ -pregnen-17-ol-3-on-21-al (II), m.p. 149—151° [dioxime, m.p. 215° (decomp.) (softens at 144°)], dehydrated in boiling AcOH containing Ac_2O to (I) [disemicarbazone, rapid decomp. $>370^\circ$], also obtained from (II) by boiling in EtCO_2H under N_2 , or in *m*-xylene containing I, by sublimation at 145°/0.0001 mm., or by treatment with anhyd. CuSO_4 at 135°/0.001 mm. (I) is oxidised by air in PhMo at 100° to $\Delta^{4:5:17:20}$ -pregnadien-3-one-21-carboxylic acid, m.p. 265—267° (decomp.) (*Me* ester, m.p. 152—154°). Boiling AcOH containing Ac_2O converts (II) into $\Delta^{4:16:20}$ -21-acetoxypregnatrien-3-one, m.p. 192—194° [also obtained similarly from (I)], with, apparently its stereoisomeride, m.p. 262—264° (decomp.). Successive treatments of $\Delta^{5:6}$ -17-allylandrostene-3t:17-diol 3-monoacetate (III) with Br in AcOH, O_3 , Zn dust, and Girard's reagent lead to $\Delta^{5:6:17:20}$ -3t-acetoxypregnadien-21-al, m.p. 185—187° (semicarbazone, m.p. 245—246°), also obtained by treating (III) successively with OsO_4 in Et_2O , Na_2SO_3 in boiling aq. EtOH, KIO_4 , and H_2SO_4 in aq. MeOH, and Ac_2O - $\text{C}_5\text{H}_5\text{N}$ at room temp. The presence of $\alpha\beta$ -unsaturated :CO suffices for the positive but relatively slow and not particularly intense reduction of AgNO_3 - NH_3 . Other substituents except CHO or ketol do not cause any reduction. A suitable reagent for the detection of CHO is 1:4- $\text{C}_{10}\text{H}_7(\text{OH})_2$, which gives a pronounced red colour with (II) but only a weak, non-sp. fluorescence with its precursor. $\alpha\beta$ -Unsaturated 3-ketones with a double linking in the 17-side-chain give a red to violet-red colour with 1:4- $\text{O}:\text{C}_{10}\text{H}_6:\text{O}$. If CO is replaced by a $\beta\gamma$ -unsaturated OH or an acyloxy-group at C_{13} , the colour is displaced towards shorter λ and becomes blue. When an alkyl residue constitutes the side-chain and the unsaturated :CO is also present in position 3 a green colour is formed which becomes blue in the case of the corresponding 3-OH-derivatives. Other compounds investigated give at most a feeble colour. H. W.

Intramolecular dehydrogenation of aromatic nuclei.—See B., 1939, 809.

Absorption spectra of naturally-occurring naphthaquinones and their derivatives.—See A., 1939, I, 402.

Chemistry of vitamin-E. VII. Preparation of quinones from methylphenols. L. I. SMITH, J. W. OPIE, S. WAWZONEK, and W. W. PRICHARD (J. Org. Chem., 1939, 4, 318—322).—The prep. of polymethylquinones is effected by coupling the requisite polymethylphenol with diazotised sulph-anilic acid, reductive cleavage of the azo-compound, and oxidation of the NH_2 -phenol followed by the removal of the quinone by steam-distillation or filtration. If certain precautions are taken pure quinones are obtained. Duroquinone, trimethylbenzoquinone, and *m*- and *p*-xyloquinone have been prepared in overall yields of 50—90% by the method, which fails when applied to the prep. of toluquinone. H. W.

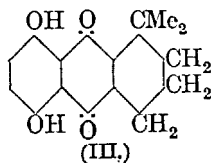
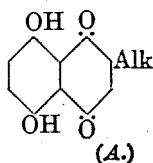
(A) Quinones having vitamin-K activity. L. F. FIESER, D. M. BOWEN, W. P. CAMPBELL, M. FIESER, E. M. FRY, R. N. JONES, B. RIEGEL, C. E. SCHWEITZER, and P. G. SMITH. (B) Synthesis of anti-hæmorrhagic compounds. L. F. FIESER, D. M. BOWEN, W. P. CAMPBELL, E. M. FRY, and M. D. GATES, jun. (J. Amer. Chem. Soc., 1939, 61, 1925—1926, 1926—1927).—(A) Vitamin-K activity of 2:3-dimethyl-1:4-naphthaquinone [absorption max. at 246 and 265 ($\log \epsilon$ 4.2—4.3) and 330 m μ . ($\log \epsilon$ 3.4)] is $<1/250$ that of pure $-K_1$. Lomatol and hydroxy-hydrolapachol are active. Diallyl-1:4-benzoquinone (I), m.p. 16°, diallylquinol (II), m.p. 130—131° [obtained with an isomeride (III), m.p. 87—90°, from quinol diallyl ether; oxidation gives (I)], the diacetate, m.p. 111—112°, of (II), lapachol, hydrolapachol, lomatol *Me* ether, m.p. 61.5—62°, and lapachol *Me* ether, m.p. 51.5—52°, have no, or only a trace of, activity. The oxido-reduction potential of $-K_1$ indicates that it is a 2:3-dialkyl-1:4-naphthaquinone. $-K_1$ may be 2-methyl- or 2:(?6)-dimethyl-3-phytyl- and $-K_2$ 2:3-difarnesyl-1:4-naphthaquinone. 2:1- $\text{CH}_2:\text{CH}:\text{CH}_2\text{C}_{10}\text{H}_6:\text{OH}$ is converted by way of the azo-compound and amine into 2-allyl-1:4-naphthaquinone (IV), m.p. 36—36.5°. 1:4-Dialloxy-naphthalene, m.p. 49.5—50°, with NPhEt_2 and Ac_2O gives 1:4-diacetoxy-2:3-diallylnaphthalene (V), m.p. 92.5—93°, which resists alkaline hydrolysis but with MgRHal and O_2 in Et_2O gives a quinone (VI), m.p. 129—130° (absorption max. at 245, 267, and 330 m μ .).

(B) 2:3-, 2:6-, and 2:7-Dimethyl-1:4-naphthaquinone have, respectively, very great, very slight, and definite $-K$ activity. Benzo- are much less active than naphthaquinones. 2-Allyl-1:4-naphthaquinone, which contains a $\beta\gamma$ -unsaturated side-chain, is particularly active; (V) is inactive. The intense absorption bands of 2:3-dialkyl-1:4-naphthaquinones have general and fine structure similar to that of $-K_1$ and $-K_2$. These facts support the structures postulated for $-K_1$ and $-K_2$. 3-Hydroxy-2- Δ^6 -heptenyl- and -2-*n*-heptyl-1:4-naphthaquinone are slightly active. 2:6:8- $\text{C}_{10}\text{H}_7\text{Me}_2:\text{O}:\text{CH}_2:\text{CH}:\text{CH}_2$ is rearranged to 3:7-dimethyl-2-allyl-1-naphthol, b.p. 152—157°/2 mm., converted into the 4- NH_2 -derivative and thence

($\text{FeCl}_3\text{-COMe}_2$) into 2 : 6-dimethyl-3-allyl-1 : 4-naphthaquinone, m.p. 42—42.5°. Ag_2O oxidises (III) to an oily quinone, which adds $(\text{CH}_2\text{CMe})_2$ to give a product, converted by isomerisation and oxidation (CrO_3) into 6 : 7-dimethyl-2 : 3-diallyl-1 : 4-naphthaquinone, m.p. 69.5—70.7°. 6 : 7-Dimethyl-1 : 4-naphthaquinone, m.p. 118—119°, is similarly prepared. The adduct of 1 : 4- $\text{O:C}_6\text{H}_4\text{:O}$ and $(\text{CH}_2\text{CH})_2$ with $\text{CH}_2\text{:CH-CH}_2\text{Br}$ and K_2CO_3 in COMe_2 gives 1 : 4-diallyloxy-5 : 8-dihydronaphthalene, m.p. 64—65°, rearranged in hot kerosene to 1 : 4-dihydroxy-2 : 3-diallyl-5 : 8-dihydronaphthalene, m.p. 108—109°, which with $\text{CrO}_3\text{-AcOH}$ gives 2 : 3-diallyl-1 : 4-naphthaquinone (VII), m.p. 29—30°. (VI) is a quinone with 2 H more than (VII); more gentle cleavage of (V) by MgMeBr and oxidation by Ag_2O gives (VII). Absorption spectra of many of these quinones are given (T. J. WEBB). The NaOEt-EtOH reaction for $-K_1$ is given by the allylnaphthaquinones (allyl group in quinone ring). R. S. C.

Constitution of vitamin- K_1 . D. W. MACCORQUODALE, S. B. BINKLEY, S. A. THAYER, and E. A. DOISY (J. Amer. Chem. Soc., 1939, 61, 1928—1929).—When hydrogenated catalytically, vitamin- K_1 absorbs 4 H_2 (3 H_2 to reduce the quinone ring; 1 H_2 to reduce the side-chain). The quinol diacetate from $-K_1$ with O_3 gives (?) $\zeta\kappa\epsilon$ -trimethylpentadecan- β -one (semicarbazone, m.p. 66—67°). CrO_3 oxidises $-K_1$ to $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and (?) 2-ethyl-1 : 4-naphthaquinonyl-3-acetic acid, m.p. 210° (decomp.). $-K_1$ is thus probably 2-ethyl-3-phytyl-1 : 4-naphthaquinone. R. S. C.

Synthesis of alkannan and other alkynaphthazarins. H. BROCKMANN and K. MÜLLER (Annalen, 1939, 540, 51—72; cf. A., 1936, 79).—Structures ascribed below are supported by absorption spectra, the main max. ($\mu\mu$.) of which (in C_6H_6) are given in parentheses. Mixed products are separated by adsorption on acid-washed SiO_2 or CaC_2O_4 . $p\text{-C}_6\text{H}_4(\text{OMe})_2$, RCOCl , and AlCl_3 in boiling CS_2 give mixed acylquinol Me_1 and Me_2 ethers (40—50%), reduced by Zn-Hg-HCl-AcOH to the alkylquinol ethers. Thus are prepared 2-isobutyrylquinol Me_2 , b.p. 160—165°/17 mm., 2-isobutylquinol Me_2 , b.p. 131—134°/20 mm., 2-isovalerylquinol Me_1 , b.p. 177—178°/18 mm., 2-isoamylquinol Me_1 , b.p. 154—156°/18 mm., 2- γ -methyl-n-valerylquinol Me_2 , b.p. 172—173°/7 mm., and 2- δ -methyl-n-amylquinol Me_2 ether (I), b.p. 168—170°/8 mm. (converted by AlCl_3 in boiling PhMe into 2- δ -methyl-n-amylquinol, m.p. 94°). With maleic anhydride (II) and $\text{AlCl}_3\text{-NaCl}$, first at 170° and then at 200° (1—2 min.), the appropriate ethers give ethyl-, m.p. 127°, n-propyl-, m.p. 98°, isobutyl-, m.p. 94°, and isoamyl-naphthazarin (A),



m.p. 89°, but (I) gives 1 : 1-dimethyl-1 : 2 : 3 : 4-tetrahydroquinizarin (III), m.p. 83° (550, 512). 2 : 3-Dimethylnaphthazarin [prep. from 2 : 3-dimethylquinol (IV) and (II)], m.p. 174° (552, 513, 481), and

$\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$ give a quinizarin derivative, $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2$, m.p. ~243—246° (496). With toluquinone or (IV), citraconic anhydride gives 2 : 6- (and/or 2 : 7-)di-, m.p. ~127° (560, 520, 485), or 2 : 3 : 6-tri-methylnaphthazarin, m.p. 165° (554, 516, 482), respectively. 2 : 3-Dihydronaphthazarin with an excess of Bu^tCHO and HCl in warm AcOH gives a diisoamyl-naphthazarin, m.p. 127° (562, 523, 487), and another product, but with 1 mol. of aldehyde gives in poor yield a product, $\text{C}_{25}\text{H}_{20}\text{O}_8$, m.p. 178°; with an excess of $\text{iso-C}_5\text{H}_{11}\text{-CHO}$ (V) or $n\text{-C}_6\text{H}_{13}\text{-CHO}$ it gives a di-(δ -methyl-n-amyl)-, m.p. 78°, or di-n-heptyl-naphthazarin, m.p. 114—115°, respectively. Naphthazarin (VI), (V), and conc. HCl in AcOH at 100° give mainly an amorphous product with some 1'-dehydroalkannan [2- δ -methyl- Δ^4 -n-pentenyl-naphthazarin] (VII), m.p. 111°, sublimes at 120—125°/0.0005 mm. (579, 534, 499), diisobutylquinizarin, m.p. 114° (469), and alkannan (VIII); under other conditions mainly (VIII) is obtained. $\text{H}_2\text{-PtO}_2$ in AcOH reduces (VII) to (VIII), whereby the structure of (VIII) is confirmed. With Bu^tCHO , (VI) gives Δ^4 -isopentenyl- (IX), m.p. 120—121°, and isoamyl-naphthazarin, m.p. 90° [obtained also by hydrogenating (IX)], and with $n\text{-C}_6\text{H}_{13}\text{-CHO}$ gives heptylnaphthazarin, m.p. 92—93°. The mechanism of the aldehyde condensations is discussed. The alkyls of the dialkynaphthazarins are probably in different rings. R. S. C.

Action of ammonia on anthraquinone in presence of reducing agents. I, II. H. SHINGU (J. Soc. Chem. Ind. Japan, 1939, 42, 173—174b).—Anthraquinone with NH_3 and $\text{Na}_2\text{S}_2\text{O}_4$ under pressure at 140—150° yields mesoanthraniline (I) (60% if 2 mols. of $\text{Na}_2\text{S}_2\text{O}_4$ are used), anthranol, dianthranol, and a N-containing ketodianthranyl (?) derivative, also produced, along with (I) (30%) and dihydrodianthrondimine (5%), from anthraquinol and NH_3 . The mechanism of the reaction is discussed. Similar reductive amination of substituted anthraquinones has been investigated. A. LI.

Synthesis of hydroxyanthraquinone salts. II. **Action of aqueous solutions of inorganic salts on hydroxyanthraquinones.** G. FLUMIANI and V. BAJIĆ (Monatsh., 1939, 72, 368—372).—Addition successively of hydroxyanthraquinone (A) (0.2), CuSO_4 (0.2), and dil. H_2SO_4 (5—10 drops) to boiling H_2O (200 g.) gives the Cu salts (A., 1938, II, 237). Salts are formed only from OH in α -positions. Salts of the type, $\text{Cu}[(A) - \text{H}]_2$, are obtained in 20—70% yield from 1 : 2-di-, 1 : 2 : 6- and 1 : 2 : 7-tri-hydroxyanthraquinone, and of the type, $\text{Cu}_2[(A) - \text{H}]_2$, from 1 : 5- and (in aq. EtOH at 80°) 1 : 4-di- and 1 : 2 : 5 : 8-tetra-hydroxyanthraquinone. Salts are not obtained from 2-hydroxy-, 2 : 6- or 2 : 7-dihydroxy-anthraquinone. R. S. C.

Biochemistry of micro-organisms. LXII. Crystalline colouring matters of species in the Aspergillus glaucus series. II. J. N. ASHLEY, H. RAISTRICK, and T. RICHARDS (Biochem. J., 1939, 33, 1291—1303).—Rubroglaucon (A., 1934, 1263; 1937, II, 106) is a mixture of physcion (I) [4 : 5-dihydroxy-7-methoxy-2-methylantraquinone], dimorphous, m.p. 203—204° (diacetate, new m.p. 186—187°), and the deep red erythroglaucon (II), $\text{C}_{16}\text{H}_{12}\text{O}_6$,

dimorphous, m.p. 205—206° [*triacetate*, m.p. 225°; *Me₃ ether* (III), m.p. 187—188°]. *Cynodontin Me₄ ether*, m.p. 233—234°, differs from (III), thus showing that (II), which is a tetrahydroxymethylanthraquinone *Me₁ ether*, is not a *cynodontin Me₁ ether*. In five of the species examined, (I) and (II) are accompanied by physcion anthranols *A*, m.p. ~260° (decomp.), and *B*, dimorphous, m.p. 181—182°; *B*, but not *A*, is obtained by reduction (Zn dust, AcOH) of (I) and both are oxidised (CrO₃-AcOH) to (I). These anthranols are probably 4 : 5-dihydroxy-7-methoxy-2-methyl-9- and -10-anthranols. Of the 17 species of *A. glaucus* examined, all give (I), (II) (except *A. mutabilis*), and flavoglaucin (except possibly *A. echinulatus*); 6 species give auroglaucin.

H. B.

d-Neoisomenthol. W. HÜCKEL and H. NIGGE-MEYER (Ber., 1939, 72, [B], 1354—1358).—*l*-Piperitone is reduced (Pd-C in Pr^oOH) to a mixture of 70% of *d*-isomenthone and 30% of *l*-menthone, which is hydrogenated (Pt sponge in AcOH) to a mixture of *d*-neoisomenthol (I), (70%), *d*-neomenthol (II) (25%), and *l*-menthone (5%); *d*-isomenthol (III) does not appear to be present. When the mixture is treated with 70% of the theoretical quantity of 3 : 5-(NO₂)₂C₆H₃·COCl in C₅H₅N, nearly all of (II), which reacts very slowly, remains unaffected. The ester obstinately retains small amounts of *l*-menthyl dinitrobenzoate. It is therefore hydrolysed and the alcohol is purified through its *p*-nitro-, *p*-amino-, and *p*-benzamido-benzoate, thereby giving (I) with all the properties recorded by Read and Grubb (A., 1934, 528). Since, in acid solution, (I) is formed almost exclusively from *d*-isomenthone (IV), it follows that the vicinal substituents are in the *cis*-position to one another, thus confirming Read's view of the configuration of (I). This is further confirmed by the observation that *d*-neoisomenthyl *p*-toluenesulphonate, m.p. 66—67°, is as unstable as the ester of (II) whereas the esters of (III) and *l*-menthol are stable. In sign and magnitude [α] of (I), but not of (III), depends greatly on the solvent. Cautious oxidation of (I) with CrO₃ in AcOH gives almost homogeneous (IV), the oxime of which is reduced to the amine, which is purified through the hydrochloride, decomp. 258°, [α]_D²⁰ +21.1° in H₂O. This is converted by HNO₂ into homogeneous (III), m.p. 83°, [α]_D²⁰ +26.5° in EtOH (*p*-toluenesulphonate, m.p. 84.5°, [α]_D²⁰ +5.88° in C₆H₆). *dl*-isoMenthon (*p*-toluenesulphonate, m.p. 64°) is most simply obtained by the hydrogenation (Ni at 140°/50—70 atm.) of thymol; the crude material is transformed into the *p*-nitrobenzoate, which is converted into the *p*-amino- and *p*-benzamido-, m.p. 119—120°, -benzoate, which is hydrolysed.

H. W.

4-Methylbornylene and its hydration. A. I. SCHAYRGIN (J. Gen. Chem. Russ., 1939, 9, 516—521).—Dehydration by the xanthate method of 4-methylborneol or 4-methylisborneol (I) yields in both cases 4-methylbornylene; this yields chiefly (I) when hydrated by the methods of Bertram and Walbaum or of Kondakov.

R. T.

Use of isotopes in chemical reactions. I. Mechanism of the Wagner-Meerwein rearrange-

ment. Exchange of radioactive chlorine and of deuterium between camphene hydrochloride and hydrogen chloride. T. P. NEVELL, E. DE SALAS, and C. L. WILSON (J.C.S., 1939, 1188—1199).—The conversion of camphene hydrochloride (I) into isobornyl chloride (II) in presence of D radio-chloride proceeds in two steps, shown by comparing the speeds of rearrangement of Cl exchange and H exchange; the first step involves the rapid establishment of an ionic equilibrium by separation of Cl, and the second a relatively slow bimol. reaction between the org. ion and HCl. Experiments in pure CHCl₃ at 0° show that rearrangement is 1/15 as fast as Cl exchange. The difference between the mechanism for rearrangement and for H exchange is that interaction of the org. ion with HCl is much slower in the former case and much faster in the latter case than the preliminary halogen ionisation. The dissociation of (I) into camphene and HCl has no direct bearing on the rearrangement except in so far as it supplies the HCl necessary for the rearrangement when this has not been initially added. The bimol. reaction of the org. ion and HCl involves a Walden inversion and it follows that (II) has the *cis*-(*exo*)-configuration. It is concluded that D exchange involves one of the bridge heads; this process cannot involve a Walden inversion and therefore substitution of H by D proceeds with retention of configuration.

F. R. S.

Action of acetic acid on α -pinene in presence of acetic anhydride and boron trioxide. I. Preparation of borneol. II. Identification of by-products. M. IMOTO (J. Soc. Chem. Ind. Japan, 1939, 42, 183—185B, 185—186B).—I. The influence of temp., quantity of AcOH and of catalyst, variation of reaction method, and the presence of dipentene or α -terpinyl acetate on the yields of bornyl and isobornyl acetate is described.

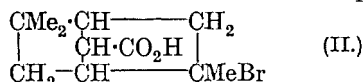
II. Dipentene, camphene (?), α -terpinene, *p*-cymene, terpinolene, and α - and β -fenchyl acetates are by-products of the reaction.

A. LI.

Camphor derivatives. III. Derivatives of camphor containing sulphur. T. TUKAMOTO (J. Pharm. Soc. Japan, 1939, 59, 37—41).— π -Thiol-*d*-camphor, m.p. 94°, [α]_D²² +108.7°, is obtained in 21.7% yield by the reduction of *d*-camphor- π -sulphonyl chloride with powdered Sn and conc. HCl at 40—50° and subsequently at 100°, or in 11.4% yield by the use of Zn dust and AcOH under similar conditions. The acetate, m.p. 34°, semicarbazone, m.p. 219—220°, Hg derivative, blackens at ~260°, and the corresponding disulphide, m.p. 215°, are described. 10-Thiol-*d*-camphor, m.p. 66° (corresponding disulphide, m.p. 231°), is obtained in 40% yield by the action of Sn and HCl on *d*-camphor-10-sulphonyl chloride; the use of Zn dust and AcOH at 100° leads to *d*-camphor. *d*-Chlorocamphor π -sulphoxide is transformed by Zn dust and AcOH at 40—50° into *trans*- π -aldehydocamphor, m.p. 195—196°, with a little π -thiol. Under identical conditions chlorocamphor ω -sulphoxide (I) affords 10-aldehydecamphor (II), m.p. 205° (semicarbazone, m.p. 249°; identification by oxidation by KMnO₄ to ketopinic acid), and a little 10-thiol (III). With Zn dust and H₂O at 100° (I) affords some (II) but no (III). Thiocamphor

(IV), m.p. 118°, is prepared by treating camphoroxime in Et₂O with NaNO₂-20% H₂SO₄, whereby a mixture of camphorimine nitrate and pernitroso-camphor results, and this is converted by conc. aq. NH₃ into camphorimine, which with H₂S in C₆H₆ at 100° yields (IV). H. W.

[Reactions of] **δ-fenchene-3-carboxylic acid**. G. A. NYMAN and E. ELOMAA (Annalen, 1939, 539, 266—275).—δ-Fenchene-3-carboxylic acid (I) (prep. from *dl*-isofenchol-3-carboxylic acid modified to give a 68% yield) adds HBr in AcOH or H₂O to give *bromofenchane-carboxylic acid* [? (II)], m.p. 138—139°, and smaller amounts of an *isomeride*, m.p. 125.5°



(decomp.), a pinacolonic rearrangement probably occurring. Removal of HBr from the Me ester by quinoline at 175—180° (followed by KOH-EtOH) or *N*-KOH-EtOH at 18° regenerates (I). Warm dil. NaOH, Na₂CO₃ at 50°, or Ag₂O at room temp. converts (II) into the corresponding *OH-acid*, m.p. 175—176°, which gives no lactone, is oxidised by HNO₃ (*d* 1.27) at 100° to an *acid*, OH·C₉H₁₃(CO₂H)₂, m.p. 226.5°, and is converted by hot HCO₂H and subsequent distillation into (I) and a *OH-acid*, C₁₁H₁₈O₃, m.p. 213°, best obtained by boiling 18% HCl. R. S. C.

Triterpenes. L. Transformation of β-boswellic acid into α-amyrin. L. RUZICKA and W. WIRZ (Helv. Chim. Acta, 1939, 22, 948—951).—β-Boswellic acid has m.p. 236—238°, [α]_D +237° in CHCl₃. Acetyl-β-boswellic acid is converted by SOCl₂ at room temp. into *acetyl-β-boswellyl chloride*, m.p. 193°, which is reduced (Pd-BaSO₄ in PhMe) to the corresponding (impure) aldehyde (oxime, m.p. 226°), which gives a marked yellow colour with C(NO₂)₄. The *semicarbazone*, m.p. 281—284° (slight decomp.), is transformed by NaOEt-EtOH at 200° into α-amyrin, m.p. 185—187°, [α]_D +91.4° in C₆H₆ (acetate, m.p. 225—226°, [α]_D +83.3° in CHCl₃; benzoate, m.p. 193—194°). H. W.

Triterpene resinols and related acids. VII. D. E. SEYMOUR, K. S. SHARPLES, and F. S. SPRING (J.C.S., 1939, 1075—1078).—Oxidation (H₂O₂) of α-amyrenyl benzoate gives a compound, m.p. 302—304° (small amount), and α-amyranonyl benzoate (I), m.p. 205—206°, [α]_D²⁵ +113.6° in CHCl₃, which is reduced (Na-C₅H₁₁·OH) to *dihydroxy-α-amyrane*, m.p. 199—201°, [α]_D²⁵ +70.5° in CHCl₃ (*diacetate*, m.p. 203—205°, [α]_D²⁵ +90.0° in CHCl₃). Br and (I) yield *iso-α-amyrenonyl benzoate*, m.p. 205—206°, [α]_D²⁵ +81.66° in CHCl₃, which when reduced (Na-C₅H₁₁·OH) and treated with Ac₂O affords α-amyradienyl acetate, identical with that prepared from α-amyrenonol; the benzoate is hydrolysed (KOH) to *iso-α-amyrenonol*, m.p. 237—238°, [α]_D²⁵ +72.11° in CHCl₃ (*Ac derivative*, m.p. 276.5°). This series of reactions emphasises the similarity in properties of the α- and β-amyrenols and points to a close structural resemblance of the unsaturated rings of these alcohols; the unsaturated centre of the α-isomeride is considerably less reactive than that of the β-isomeride. F. R. S.

Identity of pyrethrosin with chrysanthin and non-identity with geigerin. M. S. SCHECHTER and H. L. HALLER (J. Amer. Chem. Soc., 1939, 61, 1607—1609).—Pyrethrosin (I) (preferred name) (Thoms, A., 1892, 349) is identical with chrysanthin (Rose *et al.*, A., 1938, II, 239) and chrysanthin (Chou *et al.*, A., 1934, 1007). (I), C₁₇H₂₂O₅, m.p. (from EtOAc) 201° or (from EtOH) 177—178°, [α]_D²⁰ -30.5° in CHCl₃, -38.1° in abs. EtOH, reacts with 2 mols. of alkali forming AcOH and an acid, C₁₅H₂₆O₇, and gives no 2:4-dinitrophenylhydrazones. Geigerin (Rimington *et al.*, Onderstepoort J. Vet. Sci., 1936, 7, 485) differs therefrom, having double m.p. (α-form) 78° and 189°, (β-form) 68° and 169°, [α]_D²⁰ -42.58° in CHCl₃, -60.23° in abs. EtOH, giving a 2:4-dinitrophenylhydrazone, reacting with 2 mols. of alkali to give an acid, C₁₅H₂₂O₅, and differing also in reactions with HCl, H₂SO₄, Br-CHCl₃, and KMnO₄. R. S. C.

Constituents of species of *Helenium*. II. **Tenulin.** E. P. CLARK (J. Amer. Chem. Soc., 1939, 61, 1836—1840; cf. A., 1936, 1574).—*Helenium macrocephalum* contains helenalin, which is a vermifuge, fish poison, and insecticide. Extraction of *H. tenuifolium*, *H. elegans*, or *H. badium* with CHCl₃ yields, often with difficulty and in variable yield, *tenulin* (I), C₁₇H₂₂O₅, m.p. 193—195°, [α]_D²⁰ -21.6° in EtOH, which gives no reactions for OH, CO, CO₂H, or OR. H₂-PtO₂ reduces (I) in EtOAc to *dihydrotenulin*, m.p. (? + solvent) 182° (anhyd.) 172° [*phenylhydrazone*, m.p. 248° (decomp.)]. Br in EtOAc gives a *dibromide* ["*dibromotenulin*,"] C₁₇H₂₂O₅Br₂, m.p. 124—125° (decomp.), and, from the mother-liquors, after 2—3 days "*bromotenulin*," C₁₇H₂₁O₅Br, m.p. 202—203° (decomp.). When heated at 300°, (I) evolves gas and yields *anhydrotenulin*, C₁₇H₂₀O₄, m.p. 172°. With NaOAc in boiling Ac₂O, (I) gives a *substance*, C₂₂H₂₆O₅, m.p. 240°. Alkali under various conditions converts (I) into an isomeride, *isotenulin* (II), m.p. variable between 157° and 160—161° (obtained from *H. tenuifolium* by the method of Buehler *et al.*, A., 1938, III, 161), with (under some conditions) a *substance*, C₁₅H₂₀O₄, m.p. 255°. By the methods used for (I), (II) gives a *H₂-derivative*, m.p. 151° (*phenylhydrazone*, m.p. 219—220°), "*dibromo-*" [a *dibromide*], m.p. 135° (decomp.), and *bromo-isotenulin*, m.p. 213° (decomp.). One lot of *H. tenuifolium* gave (I) and a *substance*, C₁₆H₂₂O₅, m.p. 233—234° (gives RI equiv. to 3.85% of OMe; *H₂-*, m.p. 192°, and two *Ac derivatives*, m.p. 163° and 193°). R. S. C.

Constitution of forsythin. II. S. KUNIMINE and S. WADA (J. Pharm. Soc. Japan, 1938, 58, 182—185).—Nitration of *d*-forsythigenol Me ether (I) gives a (NO₂)₂-derivative, m.p. 180° [with HNO₃ affords 4:5:1:2-(NO₂)₂C₆H₂(OMe)₂], and 4:1:2-NO₂·C₆H₃(OMe)₂. Hot MeOH-HCl converts (I) into pinoresinol Me₂ ether (II) [diastereoisomeric with, and also converted by MeOH-HCl into, (I)] and *d-epiforsythigenol* Me ether (III), m.p. 133—134° [(NO₂)₂-derivative, m.p. 230°]. Fission of the CH₂O₂ group of *d*-sesamin and subsequent methylation gives (I), (II), and a compound corresponding with (III). H. B.

Isolation of elemi resin acids. M. MLADENOVIC (Monatsh., 1939, 72, 350—353).— NH_3 in wet Et_2O ppts. some, but not all, of the NH_4 salts (cryst.) of the acids from elemi resin in a very pure state. No pptn. occurs in dry Et_2O . β -Elemionic and γ -elemic acids are completely pptd., and thus it is the neutral constituents which hinder pptn. from the resin.

R. S. C.

Glycyrrhetic acid. K. TAKEDA (J. Pharm. Soc. Japan, 1938, 58, 194—197).—Glycyrrhetic acid, m.p. 292—294°, $[\alpha]_D +160.3^\circ$ in CHCl_3 (cf. lit.) [acetate, m.p. 314—317°; Me ester (I), m.p. 258°, $[\alpha]_D +154.8^\circ$ in CHCl_3 (acetate, m.p. 301—303°; *di-bromide*, decomp. 180—181°)], is obtained from K glycyrrhizate and 1% H_2SO_4 at 130—140°/3.5—4 atm. Oxidation (CrO_3 - AcOH at 50—60°) of (I) gives *Me ketoglycyrrhetate*, m.p. 251° (*oxime*, m.p. 260°; *semicarbazone*, decomp. 250°), reduced $[\text{Al}(\text{OPr}^i)_3 \text{ in } \text{PrOH}-\text{C}_6\text{H}_6]$ to (I). S. H. H.

Sweet constituents of liquorice root. G. KURONO (J. Pharm. Soc. Japan, 1938, 58, 220).—Me glycyrrhetinate and CrO_3 - AcOH give *Me ketoglycyrrhetinate*, $\text{C}_{30}\text{H}_{46}\text{O}_4$ (*oxime*, m.p. 288.5°; *semicarbazone*, m.p. 254°). Glycyrrhetic acid with Na in hot EtOH gives *dehydrohydroglycyrrhetic acid*, $\text{C}_{30}\text{H}_{46}\text{O}_3$, m.p. 287° [*Me ester*, m.p. 272°; *acetate*, m.p. 261°; unsaturated to $\text{C}(\text{NO}_2)_4$], and, when distilled at 380—400°, gives a (?) *hydrosapotalene*, $\text{C}_{13}\text{H}_{20}$, b.p. 95—100°/2 mm., converted by Se into *sapotalene*.

R. S. C.

Smilagenone: a correction. G. A. R. KON, H. R. SOPER, and A. M. WOOLMAN (J.C.S., 1939, 1201).—Smilagenone, prepared on a larger scale (cf. A., 1936, 1386), has m.p. 187—189° (lit. 157°). *o*-Bromobenzoates have been found suitable for characterisation of smilagenin (m.p. 196—197°) and sarsasapogenin (m.p. 178—179°).

F. R. S.

Identity of soja-sapogenol B with a new sterol ("sapogenol") from shoyu oil. K. TSUDA and T. KAZANO (J. Pharm. Soc. Japan, 1939, 58, 142).—Sapogenol, $\text{C}_{30}\text{H}_{50}\text{O}_3$, m.p. 258° (A., 1937, II, 417), is identical with soja-sapogenol B, m.p. 259° (Tsuda *et al.*, A., 1938, II, 24, 239).

A. T. P.

Pittosapogenin, $\text{C}_{30}\text{H}_{50}\text{O}_7$, m.p. 308—310°, $[\alpha]_D^{20} +27.8^\circ$ in CHCl_3 + MeOH (acetate, m.p. 252—254°), and compound, m.p. 51—52°, from *Pittosporum undulatum*.—See A., 1939, III, 638.

Saponins. III. Dissociation constant and potentiometric titration of sapoalbinic acid. R. RUYSSSEN and E. O. K. VERSTRAETE (Natuurwetensch. Tijds., 1939, 21, 125—136).—Sapoalbinic acid, obtained by dialysis of the saponins from soapwort, behaves like a monobasic org. acid, $\alpha = 7.05 \times 10^{-5}$ in concns. 1.25—10% from concn.- p_H and κ measurements. The results deviate at lower and higher concns. in the latter case owing to aggregation. The equiv. is const. over a wide range of concns. at 1545. Conductometric methods cannot be used for standardising solutions of saponin acids. Direct titration with indicators (phenolphthalein) of the saponin acid and the sapogenin obtained by hydrolysis shows that the CO_2H occurs only in the saponenin part of the mol.

S. C.

Sapogenins. V. Bassic acid. B. J. HEYWOOD, G. A. R. KON, and L. L. WARE. VI. **Quillaic acid.** D. F. ELLIOTT and G. A. R. KON (J.C.S., 1939, 1124—1129, 1130—1135).—V. *Bassic acid* (I), $\text{C}_{30}\text{H}_{46}\text{O}_5$, has been isolated from several species of *Bassia* and is shown to be an acid of the triterpene series; it has m.p. 316°, $[\alpha]_D +82.4^\circ$ in $\text{C}_5\text{H}_5\text{N}$ [(+ H_2O), from EtOAc ; (+ MeOH) from MeOH ; (+ BuOH) from BuOH], and forms a *Me ester* (II), m.p. 212°, $[\alpha]_D +64^\circ$ in CHCl_3 . Dehydrogenation (Se) of (I) gives *sapotalene* (1 : 2 : 7- $\text{C}_{10}\text{H}_5\text{Me}_3$), 2 : 7- $\text{C}_{10}\text{H}_6\text{Me}_2$, 1 : 8-dimethylpicene (small amount), and (?) 1 : 2 : 5 : 6- $\text{C}_{10}\text{H}_4\text{Me}_3\text{OH}$ (small amount). Br and (II) yield a *di-bromide*, m.p. 133—135°, and (II) is reduced (PtO_2 - H_2) to *Me dihydrobassate*, m.p. 172—173°. COMe_3 with (II) affords an *acetonyl* derivative, m.p. 205°, indicating that the two OH involved in its formation must be in the 1 : 3 position; one of these OH must be primary since oxidation (Cu) of (II) gives CH_2O and a neutral diketone, $\text{C}_{30}\text{H}_{44}\text{O}_4$ (2 : 4-dinitrophenylhydrazone, m.p. 184°). With Ac_2O , (II) forms *triacytylbassic acid* (+ H_2O), m.p. 117° (*Me ester*, m.p. 95—96°), and with Br- AcOH gives a *Br lactone*, m.p. 220°. The two OH, CO_2H , and a double bond in (I) occupy positions similar to those of other sapogenins but there is another OH and a reactive double bond the positions of which still remain to be determined. A partial formula for the compound is suggested.

VI. **Quillaic acid** (II), m.p. 292—293°, $[\alpha]_D +56.1^\circ$ in $\text{C}_5\text{H}_5\text{N}$, is $\text{C}_{30}\text{H}_{46}\text{O}_5$ and not $\text{C}_{29}\text{H}_{44}\text{O}_5$ (cf. Windaus *et al.*, A., 1927, 42); it forms a *Me ester*, m.p. 222—223°, $[\alpha]_D +40.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Hydrogenation (H_2 - PtO_2) of (III) gives *dihydroquillaic acid*, m.p. 315—316°, $[\alpha]_D +32^\circ$ in $\text{C}_5\text{H}_5\text{N}$, formed by the reduction of the CO, and the *Me ester*, m.p. 269—270°, affords an *acetonyl* derivative, m.p. 256—259°, indicating the presence of 1 : 3-(OH) $_2$. The H_2 -acid is unsaturated since it gives a saturated *triacytyl-lactone*, m.p. 247—249°. With AcOH-HBr , (III) forms a *diacytyl-lactone*, m.p. 260°, $[\alpha]_D -21.5^\circ$ in CHCl_3 , deacetylated to *quillaic lactone*, m.p. 315°, and oxidised (H_2CrO_4 - AcOH) to an acid, $\text{C}_{33}\text{H}_{46}\text{O}_6$, m.p. 380° (*Me ester*, m.p. 375°), and its *Ac derivative*, m.p. 278—280°; the formation of these products indicates that (III) is an aldehyde. The C_{30} acid is further oxidised (H_2CrO_4) to a neutral compound, $\text{C}_{29}\text{H}_{42}\text{O}_4$, m.p. 296—297°, $[\alpha]_D -83.5^\circ$ in CHCl_3 (*semicarbazone*, m.p. 301—302°; 2 : 4-dinitrophenylhydrazone, m.p. 298—299°), and several acids, one of which has m.p. 290—291° and gives a *Me ester*, m.p. 206°. Oxidation (H_2CrO_4) of (III) yields a neutral compound, $\text{C}_{29}\text{H}_{40}\text{O}_5$, m.p. 256—260°. These results show that (III) contains $\text{CH}(\text{OH})\cdot\text{C}\cdot\text{CHO}$, doubtless situated in ring A; the position of the second OH has not yet been determined, but it is shown that it cannot be in rings A or C. (III) is probably a hydroxygypsogenin.

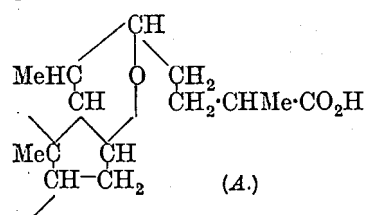
F. R. S.

Constituents of the leaves of certain *Leuca-dendron* species. II. Degradation experiments with leucodrin. W. S. RAPSON (J.C.S., 1939, 1085—1089).—Dibromoleucodrin (I) gives a series of derivatives analogous to those of leucodrin (II), and it appears as if its acidity is due to the presence

of halogen in the *m*-positions. COMe_2 and (I) afford isopropylidenedibromoleucodrin, m.p. 257° (Ac_2 derivative, m.p. 218–221°), which with $\text{CH}_3\text{N}_2\text{-MeOH}$ yields the *Me ether*, sinters 175–176°, hydrolysed to dibromoleucodrin *Me ether*, m.p. 179–180°. $\text{MeI-Ag}_2\text{O}$ with (I) gives a *Me_4 ether*, m.p. 136.5–137.5°. The action of Pb(OAc)_4 on (II) and various derivatives gives CH_2O but no other recognisable product. Acetyl isopropylideneleucodrin *Me ether* is hydrolysed to monoacetyl-leucodrin *Me ether*, m.p. 102–103°, and methylated followed by hydrolysis to isopropylideneleucodrin *Me_2 ether*, m.p. 123.5–124.5°. Leucodrin *Me_4 ether*, m.p. 123–124°, cannot be degraded with KMnO_4 but with HNO_3 gives nitro-leucodrin *Me_4 ether*, m.p. 162–163°, which with more conc. acid affords a dilactonic acid, $\text{C}_{18}\text{H}_{19}\text{O}_{11}\text{N}$, m.p. 139–140.5° (*Et ester*, m.p. 169.5–170.5°). Bromination of the *Me_4 ether* yields bromoleucodrin *Me_4 ether*, m.p. 158.5–159.5°, which with NH_3 does not form a dihydroxydiamide. Oxidation (H_2O_2) of the *Me ether* of (II) gives anisylsuccinic acid. The presence of $\geq\text{C-CH}[\text{C}_6\text{H}_4\text{-OH}(p)]\text{-CH}_2\text{-C}\leq$ in (II) seems certain. F. R. S.

Sarsasapogenin. IV. Sarsasapogenoic acid and related compounds. L. F. FIESER, E. M. FRY, and R. N. JONES (J. Amer. Chem. Soc., 1939, 61, 1849–1854; cf. A., 1939, II, 31).—Presence of C:C:CO in *Me anhydrosarsasapogenoate acetate* is confirmed by absorption max. at 243 ($\log \epsilon$ 4.13) and 303 μ . ($\log \epsilon$ 1.86) in EtOH. The absorption spectrum of the dibasic acid, $\text{C}_{27}\text{H}_{40}\text{O}_7$, indicates presence of CO but absence of C:C:CO , as does that of sarsasapogenoic acid acetate [max. at 281 μ . ($\log \epsilon$ 1.92)]; this is also so for the acid, obtained from deoxysarsasapogenin (modified prep.), and previously considered to be $\text{C}_{27}\text{H}_{40}\text{O}_4\text{-H}_2\text{O}$, but now $\text{C}_{27}\text{H}_{42}\text{O}_4\text{-H}_2\text{O}$. The formula of dehydrosarsasapogenoic acid (prep. with a substance, m.p. 202–209°, from sarsasapogenone by CrO_3 described), $\text{C}_{27}\text{H}_{40}\text{O}_5$, m.p. 164–165°, $[\alpha]_D^{25} -105^\circ$ in EtOH (*Me ester*, m.p. 125–126°, $[\alpha]_D^{25} -101^\circ$ in EtOH; with $\text{H}_2\text{-PtO}_2$ in AcOH gives in poor yield a product, m.p. $\sim 200^\circ$; unstable to alkali), is confirmed. “Anhydrotetrahydrosarsasapogenoic acid” (*loc. cit.*) may be (A). Tschesche and

Hagedorn's formula for sarsasapogenin (cf. *loc. cit.*) is held to account for the effects of acid, whilst Marker's formula (A., 1939, II, 276) does not accommodate the results of oxidation and the evidence in its favour is largely negated by the following results. Octahydro-2:2'-difuryl [prep. from 2:2'-difuryl by H_2 -Raney Ni at 150°, but not by $\text{H}_2\text{-PtO}_2$ or $\text{H}_2\text{-Pd-C}$ (cf. Kondo *et al.*, J. Pharm. Soc. Japan, 1935, 55, 142)], b.p. 77–80°/13 mm., reacts slowly with Br and a little HBr in AcOH, and (unless freshly purified) reduces SeO_2 and absorbs H_2 (PtO_2 ; HCl-EtOH), and suffers fission of one ring by HCl-AcOH at 88° giving a glycol (*bis*-3:5-dinitrobenzoate, *cryst.*). Tetrahydro-furoamide, m.p. 65–76° b.p. 135–138°/10 mm., and



MgMeCl give 2-acetotetrahydrofuran, b.p. 52.3–54.8°/10 mm. (2:4-dinitrophenylhydrazones, orange, m.p. 122–124°, and yellow, m.p. 135–136°), which is unstable to alkali. R. S. C.

Sterols. LXVII. Sarsasapogenin derivatives. Bromo-compounds. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 1921–1922).—Sarsasapogenin (I) and Br in AcOH containing a trace of HBr give bromosarsasapogenin, $\text{C}_{27}\text{H}_{43}\text{O}_3\text{Br}$, decomp. $\sim 125^\circ$, which is oxidised by CrO_3 in 80% AcOH to bromosarsasapogenone, m.p. 191° (decomp.), also obtained by brominating sarsasapogenone, which, however, with more Br gives dibromosarsasapogenone, m.p. 190° (decomp.). Reduction of bromosarsasapogenin acetate by $\text{Na-C}_5\text{H}_5\text{-OH}$ or -EtOH gives (I), by $\text{H}_2\text{-PtO}_2$ in AcOH at 70°/3 atm. gives di- and by Zn-Hg-HCl gives tetra-hydrosarsasapogenin. Boiling $\text{C}_5\text{H}_5\text{N}$ or $\text{AgNO}_3\text{-C}_5\text{H}_5\text{N}$ at 25° has no effect on (II). R. S. C.

alloStrophanthidin. E. BLOCH and R. C. ELDERFIELD (J. Org. Chem., 1939, 4, 289–297).—Evidence is adduced in favour of the view that the isomerisation involved in the allomerisation of cymarins consists in an inversion of one of the asymmetric centres of the strophanthidin mol., probably at C_{14} but possibly at C_{17} . *alloStrophanthidin* is oxidised by KMnO_4 in COMe_2 at 5° to *allotrophanthidinic acid*, $\text{C}_{23}\text{H}_{32}\text{O}_7$, m.p. 247°, $[\alpha]_D^{25} +39.2^\circ$ in MeOH, the *Me ester*, m.p. 263–265°, of which is converted by CrO_3 in AcOH into *Me allotrophanthidonate*, m.p. 258°, $[\alpha]_D^{25} +20.1^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (*Me strophanthidonate* has m.p. 161–162°, $[\alpha]_D^{25} +26^\circ$ in $\text{C}_5\text{H}_5\text{N}$). This is transformed by boiling MeOH–10% HCl into *Me monoanhydroallostrophanthidonate*, m.p. 138–145°, $[\alpha]_D^{25} +118^\circ$ in $\text{C}_5\text{H}_5\text{N}$. *Dianhydroallostrophanthidin*, m.p. 172–175°, $[\alpha]_D^{25} -123.1^\circ$ in $\text{C}_5\text{H}_5\text{N}$, obtained by the action of EtOH–HCl on dianhydroallostrophanthidin oxidoethylal, is rapidly converted by conc. HCl into a *Cl*-derivative, m.p. 165°, transformed by NH_3 in boiling EtOH into dianhydroallostrophanthidin. *alloStrophanthidin* is converted by HCl (*d* 1.19) at 0° into an unstable *Cl*-derivative, $\text{C}_{23}\text{H}_{31}\text{O}_5\text{Cl}$, m.p. 175°, transformed by $\text{NH}_3\text{-EtOH}$ into *anhydroallostrophanthidin*, m.p. 205°, $[\alpha]_D^{25} +119^\circ$ in EtOH (3-*Bz* derivative, m.p. 252°; *oxime*, m.p. 182°). H. W.

Amber. V. L. SCHMID and W. HOSSE (Monatsh., 1939, 72, 290–302).—Amber is extracted with EtOH. The extract is partly sol. in light petroleum and the dissolved portion is pptd. from the solution by MeOH. After treatment with Na_2CO_3 the material is purified chromatographically (Al_2O_3 in C_6H_6). The substance, m.p. 140°, $[\alpha]_D^{25} +58^\circ$ in C_6H_6 , thus obtained is hydrolysed by KOH–MeOH to a resin acid, $\text{C}_{25}\text{H}_{40}\text{O}_4$, m.p. 136–139°, $[\alpha]_D^{25} +29^\circ$ in C_6H_6 (*Me ester*, m.p. 125–127°; *Ac derivative*, m.p. 96–98°), and a resin alcohol (I), $\text{C}_{25}\text{H}_{36}\text{O}_2$, m.p. 117°, $[\alpha]_D^{25} +45.7^\circ$ in C_6H_6 (*acetate*, m.p. 55–56°), which slowly gives a yellow colour with $\text{C(NO}_2)_4$ and is dehydrogenated by Se at 260–280° and then at 350° to 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$ and pimanthrene (II). The portion of amber which remains in Et₂O after removal of the acids when purified chromatographically gives two fractions, m.p. 110–130°, $[\alpha]_D^{25} +34.7^\circ$ in C_6H_6 and $[\alpha]_D^{25} +26.7^\circ$ in C_6H_6 , respectively, the former of which is dehydrogen-

ated by Se to agathaline and (II). Either fraction when hydrolysed by alkali gives a resin acid, m.p. 130—135°, $[\alpha]_D^{25} + 47.2^\circ$ in C_6H_6 (*Me* ester, m.p. 120°; *Ac* derivative, m.p. 98°, $[\alpha]_D^{25} + 52.8^\circ$ in C_6H_6), and an alcohol, m.p. 113—115°, $[\alpha]_D^{25} + 45.7^\circ$ in C_6H_6 (acetate, m.p. 56—58°, $[\alpha]_D^{25} + 62.6^\circ$ in $COMe_2$), which slowly affords a yellow colour with $C(NO_2)_4$ and does not depress the m.p. of (I). H. W.

Amber. VI. Acids occurring in amber. L. SCHMID [with T. LENZER and E. BLUM] (*Monatsh.*, 1939, 72, 311—321).—Prep. of amorphous succinabietinolic (I), $OH \cdot C_{35}H_{50-52}O_3 \cdot CO_2H$, m.p. 125—128°, $[\alpha]_D^{25} + 26.34^\circ$ in $EtOH$, and succoxyabietic acid (II), m.p. ~92—95°, $[\alpha]_D^{25} + 16^\circ$ in $EtOH$, from amber is described (cf. Schmid *et al.*, A., 1933, 831). (I) gives a *Ag* salt, sensitive to light, contains 2 active H, cannot be acetylated, gives no CO-reactions, is unaffected by H_2 -PtO₂ in $AcOH$, and thus does not contain $CO \cdot C \cdot C$. It gives a *Me* ester, m.p. 82—85°, hydrolysed by 5% KOH - $MeOH$ to a different acid, m.p. 121—124°, which is also obtained from (I) by alkali. (II) is a mixture; methylation does not stop at the CO_2H . With Se at 260—350°, (II) gives $(CH_2 \cdot CO_2H)_2$ and 1 : 2 : 5- $C_{10}H_5Me_3$, but (I) gives also pimanthrene. As (I) and (II) are very sensitive to O_2 , all the products hitherto isolated from amber may be decomp. products. R. S. C.

Acid, m.p. 133°, isomeric with marindinin, from *Piper methysticum*.—See A., 1939, III, 734.

Gibberellin-A, m.p. 194—196°, and -B, m.p. 245—246° (decomp.), $[\alpha]_D^{25} + 36.13^\circ$ in $MeOH$, from rice fungus.—See A., 1939, III, 627.

Neutral substance, $C_{16}H_{26}O$, m.p. 190°, from *Asclepias syriaca*, L.—See A., 1939, III, 639.

Constitution of crystalline constituent of the bark and leaves of *Abies mariesii*, Mast. I. T. TAKAHASHI (*J. Pharm. Soc. Japan*, 1938, 58, 273—276).—Warm $EtOAc$ extracts from the bark and leaves a compound (I), $C_{30}H_{44}O_3$, m.p. 255°, $[\alpha]_D^{25} - 96.93^\circ$ in $CHCl_3$ [amorphous *tetrabromide*, m.p. ~130° (decomp.)], which is a lactone and contains OMe and $CHMe$. It is reduced (H_2 , Pt-black, $EtOAc$) to a H_2 -derivative, m.p. 225°; in Et_2O , H_4 , m.p. 206—207°, and H_8 , m.p. 191—193°, -derivatives result. Hydrolysis (0.5N- $EtOH$ - KOH) of (I) gives an amorphous *OH-acid* (II), $C_{29}H_{45}O_2 \cdot CO_2H \cdot H_2O$, m.p. 85—90° (decomp.) (K salt), another acid, m.p. ~120° (decomp.), and a neutral substance, m.p. 122—123°. Hot Ac_2O converts (II) into (I); Br - $AcOH$ gives a *tetrabromide*, m.p. ~125° (decomp.), whilst NH_2OH affords a compound, $C_{30}H_{49}O_4N_3$, m.p. 186°, insol. in cold 20% H_2SO_4 or 30% KOH . Boiling 2% $EtOH$ - HCl converts (I) into an *isomeride*, m.p. 215°, whilst 0.5N- $EtOH$ - or 0.05N- $MeOH$ - H_2SO_4 gives an *isomeride*, m.p. 24° (? 224°). Oxidation of (I) with CrO_3 ($= 3.8 O_2$) in $AcOH$ at 55—60° affords an amorphous *OMe-free acid*, $C_{20}H_{32}O_3$, m.p. ~130° (decomp.), and a diketonic *OMe-lactone*, $C_{28}H_{38}O_5$, m.p. 218—221° (*dioxime* (+ NH_2OH), m.p. ~130° (decomp.); *di-bromide*, m.p. 145—150° (decomp.), whence it is inferred that (I) contains 2 double linkings]. Oxidation ($KMnO_4 = 3 O_2$) of (I) gives $H_2C_2O_4$ and a *OMe-lactone*, $C_{28}H_{42}O_4$, m.p. 90—95° (decomp.), which is

further oxidised by CrO_3 (1.5 mols.) in $AcOH$ to an acid, $C_{20}H_{30(32)}O_5$, m.p. 135—140° (decomp.); $KMnO_4$ ($= 5.8 O_2$) in $AcOH$ at ~70° oxidises (I) to a *OMe-acid*, $C_{28}H_{42}O_5$, m.p. 215° (? *Ac*₁ derivative, m.p. 242—243°). H. B.

Constituents of "senso." VII. New constituent of native toad poison: F_3 -bufotalin. H. KONDO and S. OHNO (*J. Pharm. Soc. Japan*, 1938, 58, 102—103).—In addition to compounds previously described (cf. A., 1938, II, 197), toad poison contains *F_3 -bufotalin*, $C_{24}H_{32}O_5$, m.p. 243—245°. (Cf. A., 1939, II, 382.) E. W. W.

Constituents of "senso." VIII. Ozonisation of acetyl- ψ -deacetylbufotalin. IX. Cino-bufotalidin, a substance accompanying cino-bufagin. H. KONDO and S. OHNO (*J. Pharm. Soc. Japan*, 1938, 58, 232—234, 235—237).—VIII. The δ -lactone structure of ψ -deacetylbufotalin is confirmed by conversion of its *Ac* derivative by O_3 in $CHCl_3$ into CH_2O , HCO_2H , and $H_2C_2O_4$ [proof of $CR \begin{smallmatrix} \text{CH} \cdot C(OH) \\ \text{CH} \text{---} O \end{smallmatrix} CO$] with an α -keto-aldehyde (I), $C_{23}H_{34}O_6$, and an α -keto-acid (II), $C_{23}H_{34}O_7$. With $NH_2 \cdot CO \cdot NH \cdot NH_2$, (I) gives a *triazine*, and with AcO_2H , followed by H_2O_2 , gives an amorphous acid (III), $C_{20}H_{32}O_5$, also obtained from (II) by H_2O_2 . When kept in acid, (II) gives an aldehyde, $C_{22}H_{34}O_5$ (*oxime*). The *Me* ester of (III) yields the amide only incompletely; when treated with $MgMeI$, heated in xylene at 100—120°, and then ozonised, it yields $COMe_2$ and the cyclic ketone, $C_{19}H_{30}O_4$ (*oxime*).

IX. Cinobufagin, isolated from "senso," is accompanied by *cino-bufotalidin* (IV), $C_{24}H_{34}O_6$, m.p. 217° (decomp.) (*acetylanhydro-derivative*, m.p. 209—210°; *p-nitrobenzoate*, m.p. 236—238°), from which it is separated mechanically. A δ -lactone group is indicated in (IV) by an absorption max. at 290—300 μ . When sublimed at 0.0005 mm., (IV) gives 2 H_2O and two unsaturated $[C(NO_2)_4]$ substances, $C_{24}H_{30}O_4$, m.p. 125—128° and ?, and thus contains 2 *tert.* OH. R. S. C.

Lichen pigments of the pulvinic acid series.

V. Synthesis of *m*-hydroxypulvinic anhydride. M. ASANO and S. FUZUWARA (*J. Pharm. Soc. Japan*, 1939, 59, 83—85).—*Et* phenylecyanopyruvate and *m*- $OMe \cdot C_6H_4 \cdot CH_2 \cdot CN$ are condensed by $NaOEt$ - $EtOH$ to *m*-methoxydiphenylketipinodinitrile (I), m.p. 207.5° (decomp.), converted by the successive action of $AcOH$ in boiling 60% H_2SO_4 and Ac_2O into *m*-methoxypulvinic anhydride, m.p. 171—173°, which is demethylated by HI (d 1.7) in boiling $AcOH$ to *m*-hydroxypulvinic anhydride (II), m.p. 255—256° (acetate, m.p. 202—205°). (II) is obtained directly from (I) by the action of HI (d 1.7) in boiling $AcOH$. H. W.

Components of resins. XIII. Constitution of hinokiöl. G. FUKUI and T. CHIKAMORI (*J. Pharm. Soc. Japan*, 1939, 59, 86—91).—Methylhinokiöl is oxidised with CrO_3 and the resulting ketone is reduced (Clemmensen or Wolff-Kishner) to a yellow liquid, b.p. 170—173°/3 mm., which is dehydrogenated (Se) to methoxyretene (I), m.p. 80°. Reduction of hinokione (II) (Clemmensen) and dehydrogenation of the product yields hydroxyretene (II), m.p. 179—

180°, methylated to (I). The OH of (II) is that which was originally present in hinokiol as $\cdot\text{CH}_2\cdot\text{OH}$. $\text{K}_3\text{Fe}(\text{CN})_6$ is without action on (III). Dehydrogenation of hinokiol (IV) with Cu powder affords (II). (IV) is therefore at diterpene alcohol with a phenolic nucleus. Application of the isoprene rule leads to a modification of the formula of (IV) from $\text{C}_{19}\text{H}_{28}\text{O}_2$ to $\text{C}_{20}\text{H}_{30}\text{O}_2$. Hence (IV) is a dihydroxydimethyloctahydroretene, the nucleus and side-chains of which are derived from four isoprene residues. In addition to (IV) and hinokinin, cupressus resin yields (II). H. W.

Constitution of clerodin, the active bitter principle of *Clerodendron infortunatum*. II. H. N. BANERJEE (Trans. Bose Res. Inst., 1936—1937, 75—88; cf. A., 1938, II, 288).—The following reactions of clerodin are described. Reduction (H_2 -Pt in cyclohexane-AcOH, or Zn + AcOH) yields *dihydroclerodin*, m.p. 115° (decomp., shrinks at 80°). MgMeI in amylether gives 1 mol. of CH_4 per mol. 10% H_2SO_4 at 100° yields the compound obtained (*loc. cit.*) by hydrolysis with EtOH-KOH . Cold conc. HCl removes the Ac group, giving a compound, $\text{C}_{11}\text{H}_{15}\text{OCl}$, m.p. >360°, containing no active H. Fusion with KOH at 200° yields an amorphous substance (decomp. 360°; unaffected by CH_2N_2), further fusion of which at 250—300° affords an acid, m.p. 90—91°, equiv. wt. 104. Zn dust at 250—360° in a current of H_2 yields first a green liquid (I) (C 90.0, H 10.0%) [picrate, m.p. 131°; nitrate (containing N 8.2%), m.p. 88°], and later a brown, viscous oil. Dehydrogenation with S yields a product, b.p. 200°/20 mm., which when treated with conc. HNO_3 , reduced, diazotised, and coupled with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ yields a scarlet dye, whilst Se at 170° yields (I). Oxidation with KMnO_4 in COMe_2 yields an aromatic monobasic acid (II), $\text{C}_{13}\text{H}_{16}\text{O}_4$, m.p. 265° (decomp.); HNO_3 gives CO_2 , $\text{H}_2\text{C}_2\text{O}_4$, and a NO_2 -derivative (C 61.2, H 7.1, N 7.2%), m.p. 206°, sol. in alkali, whilst CrO_3 yields (II) and an impure substance, m.p. 117—120°, $[\alpha]_D -21^\circ$. It is concluded that clerodin contains an unsaturated ring. A. LI.

Echinochrome and spinochrome. Methoxy-derivatives. Distribution. Associated pigments. R. GLASER and E. LEDERER (Compt. rend., 1939, 208, 1939—1942).—Excess of echinochrome (I) (cf. A., 1938, II, 448) with CH_2N_2 gives *mono-*, m.p. 191°, *di-*, m.p. 161°, and *tri-methoxyechinochrome*, m.p. 137°, separated by chromatographic adsorption on CaCO_3 . Spinochrome (II) similarly yields *mono-*, *di-*, and *tri-methoxyspinochrome*, m.p. 176°, 265°, and 147°, respectively. The pigment in the ovaries of *Arbacia aequituberculata* is mainly (I), which also occurs in small amounts [with (II)] in the violet scales of *Strongylocentrotus lividus*. In the former *isoechinochrome*, m.p. 247°, and an unidentified pigment are also found. The latter contains (II) together with brown pigments which give colour reactions with FeCl_3 . J. L. D.

Scission of hydrofuran and hydropyran rings with acetic anhydride. R. PAUL (Bull. Soc. chim., 1939, [v], 6, 1162—1173; cf. A., 1939, II, 274). Orientation of the unsaturated OAc compounds (*loc. cit.*) is determined by identifying the R-CHO after treating the ozonide with Zn (+ AgNO_3). 2-

Methyltetrahydropyran and $\text{Ac}_2\text{O-ZnCl}_2$ at 200° give $\alpha\epsilon$ -diacetoxyhexane, b.p. 125—127°/14 mm., and α -acetoxy- Δ^8 -hexene, b.p. 73°/20 mm. (gives MeCHO). 2-Propyltetrahydropyran similarly gives $\alpha\epsilon$ -diacetoxyoctane, b.p. 153—155°/20 mm., and a mixture, b.p. 96—97°/14 mm., of α -acetoxy- Δ^8 - and - Δ^6 -octene (gives EtCHO + PrCHO). 2-Butyltetrahydropyran affords a mixture, b.p. 117°/20 mm., of α -acetoxy- Δ^8 - and - Δ^6 -nonene. 2-Phenyltetrahydropyran gives mainly Ph_2 (*loc. cit.*). Tetrahydrofuran and $\text{Ac}_2\text{O-ZnCl}_2$ at 230° (8 hr.) give $\alpha\delta$ -diacetoxybutane, b.p. 229—230°, or 108°/10 mm., and a fraction, b.p. 160—165°/10 mm. 2-Ethyltetrahydrofuran, at 200°, affords $\alpha\delta$ -diacetoxyhexane, b.p. 123—125°/14 mm., and α -acetoxy- Δ^8 - + - Δ^6 -hexene, b.p. 72—73°/20 mm. (gives MeCHO + EtCHO). 2-Butyltetrahydrofuran gives $\alpha\delta$ -diacetoxyoctane, b.p. 142—158°/13 mm., and a mixture, b.p. 94—95°/13 mm., of α -acetoxy- Δ^8 - (88%) and - Δ^6 -octene (22%); amyltetrahydrofuran affords $\alpha\delta$ -diacetoxy-nonane and a mixture, b.p. 117—118°/20 mm., of α -acetoxy- Δ^8 - and - Δ^6 -nonene. 2-Benzyltetrahydrofuran (at 190°) gives $\alpha\delta$ -diacetoxy- ϵ -phenylpentane, b.p. 196—197°/16 mm., and a mixture, b.p. 153—158°/14 mm., of α -acetoxy- ϵ -phenyl- Δ^6 - and - Δ^8 -pentene (hydrogenated to α -acetoxy- ϵ -phenylpentane, b.p. 153°/12 mm.). A. T. P.

Action of hydroxymethylamides on ethyl pyromucate. G. B. MARINI (Gazzetta, 1939, 69, 340—344).— $\text{o-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{OH}$ added to Et pyromucate (I) in conc. H_2SO_4 gives 5'-carbethoxyfurfurylphthalimide, m.p. 118°, hydrolysed (NaOH-EtOH) to 5'-carboxyfurfurylphthalamic acid, m.p. 204°. With $\text{NHBz}\cdot\text{CH}_2\cdot\text{OH}$, (I) gives 5'-carbethoxy-, m.p. 106°, hydrolysed to 5'-carboxy-benzfurfurylamide, m.p. 180°, and with $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, 5-carbethoxychloroacetfurfurylamide, m.p. 90°, hydrolysed by HCl to 5-carboxyfurfurylamine hydrochloride, m.p. 245° (platinichloride, m.p. 202°). E. W. W.

Aldehyde-acids and aldo-enol-lactones. I. Condensation of aconic acid with aldehydes and ketones. M. M. SCHEMJAKIN and I. A. REDKIN (J. Gen. Chem. Russ., 1939, 9, 442—446).—Aconic acid condenses with aldehydes in presence of NH_4Et_2 , at 105°, to yield benzylidene-, m.p. 201—202°, *nitrobenzylidene-*, not melting at 290°, and *furfurylidene-aconic acid*, not melting at 290°. R. T.

Vitamin-E. IV. Synthesis of tocopherols. L. I. SMITH and H. E. UNGNADE. V. Direct allylation of phenols and quinols. VI. Addition of dienes to phenols and quinols. L. I. SMITH, H. E. UNGNADE, H. E. HOEHN, and S. WAWZONEK (J. Org. Chem., 1939, 4, 298—304, 305—310, 311—317).—IV. Passage of HBr into phytol containing anhyd. Na_2SO_4 at 0° gives phytol bromide (I), which decomposes when kept at room temp. and cannot be distilled since it is largely converted at 75° into phytadiene (II). (I) when heated with trimethylquinol (III) affords some (II) and *r- α -tocopherol*, b.p. 140°/10⁻⁶ mm. (*allophanate*, m.p. 157—160°), which readily oxidises when exposed to air. Its absorption spectrum is nearly indistinguishable from that of natural α -tocopherol. *p-Xylotocopherol*, b.p. 145—150°/10⁻⁶ mm., when pyrolysed at 355—360 under CO_2 gives a mixture of quinols. *m-Xylotocopherol*,

b.p. 120—130°/10⁻⁶ mm., could not be obtained pure. These tocopherols have vitamin-*E* activity.

V. Allyl bromide (V) is less, and geranyl bromide more, reactive than $\gamma\gamma$ -dimethylallyl bromide (V) or (I) towards polyalkylphenols and quinols. (IV), (V), and (I) react with quinol in a sealed tube at 100—150° without solvent or catalyst. ZnCl₂ and C₆H₆ or light petroleum may be used but the yield and quality of the product are not improved. The optimum temp. is 100—150°; the pure materials must be thoroughly mixed to a paste and the tube heated in a vertical position. The following are described: 5-hydroxy-2:4:5:7-tetramethylcoumaran, m.p. 130.5—131.5° (acetate, m.p. 72.5—73.5°), also obtained by reducing 5-hydroxy-2:4:5:7-tetramethylcoumarone (H₂-Raney Ni at 200°/2600 lb.); 6-hydroxy-2:2:5:7:8-pentamethylchroman, m.p. 94—94.5° (acetate, m.p. 92.5—93.5°); 2:3:5-trimethylphenyl allyl ether, b.p. 59.2°/0.1 mm.; 2:3:5-trimethyl-6-allylphenol, m.p. 49.5—50.5°; 2:4:6:7-tetramethylcoumaran, b.p. 142—144°/29 mm.

VI. The condensation between dienes and phenols leading to chromans has been extended to certain quinols and to *p*-OH·C₆H₄·OMe. Under proper conditions these substances give good yields of chromans but, unless the conditions are carefully regulated, mixtures result. *p*-C₆H₄(OH)₂ does not react under any of the conditions tried; *p*-OH·C₆H₄·OMe and (III) react readily but 2:5-dimethylquinol does not. 2:3:5-C₆H₂Me₃·OH and isoprene in AcOH saturated with HCl at 0° give a phenol, C₁₄H₂₀O, m.p. 84—86°, and 2:2:5:7:8-pentamethylchroman, m.p. 40—41° (also obtained by use of ZnCl₂ as catalyst). *p*-OH·C₆H₄·OMe and dimethylbutadiene in AcOH saturated with HCl at 0° afford 6-methoxy-2:2:3-trimethylchroman, b.p. 50—53°/10⁻⁶ mm., whilst isoprene gives 6-methoxy-2:2-dimethylchroman, b.p. 74—80°/0.1 mm., and γ -chloro- α -o-hydroxy-m-methoxyphenylbutane, b.p. 83—90°/0.1 mm. (III) and isoprene in AcOH containing ZnCl₂ at 100° give 6-hydroxy-2:2:5:7:8-pentamethylchroman, m.p. 94—94.5° [acetate, m.p. 92.5—93.5°; allophanate, m.p. 209—211.5° (decomp.)]. (II) and (III) in boiling AcOH-HCO₂H afford α -tocopherol, apparently contaminated with a liquid of high b.p. H. W.

Vitamin-*E*. X. Reaction between quinones and metallic enolates. IX. L. I. SMITH and W. W. PRICHARD (J. Org. Chem., 1939, 4, 342—350).—Addition of 1:3:5:2-C₆H₂Me₃Ac followed by trimethylbenzoquinone (I) to MgEtBr in Et₂O gives 3:6-dihydroxy-2:4:5-trimethylphenylacetomesitylene, m.p. 148—148.5° (yield 90%) (diacetate, m.p. 169—170°), which does not give ketonic derivatives. It could not be converted into the corresponding coumarone by loss of H₂O. When refluxed with HCl in MeOH, EtOH, or AcOH it appears to give the *Me* ether, m.p. 158—159°, *Et* ether, m.p. 160—161.5°, and acetate, m.p. 149.5—150.3°, of the corresponding enol. When warmed with H₂SO₄ it gives only tarry products. CH₂Br·CO·CMe₂·CO₂Et could not be converted into the enolate by MgPhBr, Mg mesityl bromide, or CdPhCl, the product invariably failing to condense with the quinone. Et₂ β -keto- α -dimethylglutarate does not condense with (I) in presence of Mg(OMe)₂ and,

although it reacts with Na, the product gives only a red oil with (I). CN·CH₂·CO·CMe₂·CO₂Et with Mg(OMe)₂ affords a cryst. enolate, which gives only a non-cryst. product with (I). CHBu^t(CO₂Et)₂ reacts readily with (I) in presence of NaOEt or Mg(OEt)₂ but Bu^t is lost and the product is 5-hydroxy-2-carboethoxy-4:6:7-trimethylisocoumaranone, m.p. 111—112° (acetate, m.p. 101—103°). This is transformed by hot AcOH saturated with HCl into 5-hydroxy-4:6:7-trimethylisocoumaranone, m.p. 195—196° (acetate, m.p. 166—167°). H. W.

Vitamin-*E*. XI. Introduction of the *p*-hydroxy-group into chromans and coumarans. L. I. SMITH, H. H. HOEHN, and H. E. UNGNADE (J. Org. Chem., 1939, 4, 351—357).—2:2:5:7:8-Pentamethylchroman (I) couples very slowly with diazotised *p*-NH₂·C₆H₄·SO₃H so that only traces of the N₂ compound can be prepared. HNO₃ in AcOH readily transforms (I) into 6-nitro-2:2:5:7:8-pentamethylchroman, m.p. 125—125.5°, which is very inert and could not be reduced by Sn and HCl or by H₂ in presence of Pt at 45 lb. pressure; it is attacked by Na and Bu^tOH, giving a non-cryst. product with a marked phenolic reaction. Br in CCl₄ converts (I) into 6-bromo-2:2:5:7:8-pentamethylchroman, m.p. 69—70°, which is mixed with EtBr and dropped on to Mg; the product is transformed by O₂ into 6-hydroxy-2:2:5:7:8-pentamethylchroman, m.p. 94—94.5°, in poor yield. Similarly 5-bromo- is converted into 5-hydroxy-2:4:6:7-tetramethylcoumaran, which with alkali at 300° gives 2:3:5-C₆H₂Me₃·OH. H. W.

Vitamin-*E*. XII. Preparation of chromans by action of Grignard reagents on dihydrocoumarins. L. I. SMITH, H. E. UNGNADE, and W. W. PRICHARD (J. Org. Chem., 1939, 4, 358—362).—Under any of the conditions used the first isolable product of the action of MgEtBr on dihydrocoumaran is α -hydroxyphenyl- γ -ethylpentan- γ -ol, m.p. 71—72°, usually accompanied by and readily cyclised (boiling AcOH-20% H₂SO₄) to 2:2-diethylchroman, b.p. 128.5—128.9°/12 mm. Similarly MgPhBr affords the corresponding carbinol and 2:2-di-*n*-propylchroman, b.p. 153—154°/15 mm., but no ketone. 6-Hydroxy-5:7:8-trimethyl-3:4-dihydrocoumarin gives the unstable carbinol, readily cyclised to 6-hydroxy-2:2:5:7:8-pentamethylchroman. H. W.

Synthesis of 4-methylcoumarin derivatives, using metallic chlorides as condensing agent. Z. HORII (J. Pharm. Soc. Japan, 1939, 59, 59—60).—*m*-C₆H₄(OH)₂, 1:2:3- or 1:3:5-C₆H₃(OH)₃ with CH₂Ac·CO₂Et, using FeCl₃, SnCl₄, or TiCl₄ as condensing agent, gives 7-hydroxy-, 7:8- and 5:7-dihydroxy-4-methylcoumarin, respectively. High yields are claimed in most cases. A. T. P.

Dibenzfuran. XI. Substituents in the 4-position. H. GILMAN and P. R. VAN ESS. XII. Metalation of bromo-derivatives. H. GILMAN, H. B. WILLIS, and J. SWISLOWSKY (J. Amer. Chem. Soc., 1939, 61, 1365—1371, 1371—1373; cf. A., 1939, II, 276).—XI. Some 4-substituted dibenzfurans are prepared. Structures are proved by synthesis of any isomerides previously unknown. 3-Hydroxydibenz-

furan (I) (prep. in 56–75% yield from 3-bromodibenzfuran, CuSO_4 , Cu turnings, Cu bronze, and aq. NaOH in a steel bomb at 240°) and Br-AcOH give 4-bromo-3-hydroxydibenzfuran, m.p. 123–123.5° [Me ether (II), m.p. 117–118°], and traces of the 2-Br-derivative (isolated as the Me ether). 3-Methoxydibenzfuran [prepared from (I) by Me_2SO_4 -NaOH], m.p. 46–47°, b.p. 164–165°/6 mm., and Br-AcOH give 2-bromo-3-methoxydibenzfuran (III) (33%), m.p. 171–172°, and (II). 2-Bromo-3-acetamidodibenzfuran (prep. in 16.4% yield by bromination) and, best (96%), KOH-EtOH give the 3- NH_2 -compound, the diazonium salt from which with boiling, aq. CuSO_4 affords 13% of 2-bromo-3-hydroxydibenzfuran, m.p. 143–144° [Me ether = (III)]. $\text{CH}_2\text{:CH-CH}_2\text{Br}$, (I), and K_2CO_3 in COMe_2 give 72–82% of 3-allyloxydibenzfuran, b.p. 178–180°/4 mm., rearranged by heating at 220–230° to 3-hydroxy-4-allyldibenzfuran (IV), m.p. 83°, b.p. 173°/5 mm., which gives (Me_2SO_4) the Me ether, m.p. 67–68°, obtained also from the Mg derivative of (II) by $\text{CH}_2\text{:CH-CH}_2\text{Br}$. Hot KOH-MeOH converts (IV) into 3-hydroxy-4-propenyldibenzfuran, m.p. 94–95°. The Grignard reagent from (III) and $\text{CH}_2\text{:CH-CH}_2\text{Br}$ (excess) yield 3-methoxy-2-allyldibenzfuran, b.p. 158–159°/4 mm. Passage of O_2 over the Grignard reagent from (II) and MgBu^nBr in $\text{Et}_2\text{O-C}_6\text{H}_6$ gives 71% of 4-hydroxy-3-methoxydibenzfuran, m.p. 111–111.5°, unstable in alkali, decomposed by HI, and converted by $\text{MeI-K}_2\text{CO}_3$ - COMe_2 into 3:4-dimethoxydibenzfuran, m.p. 79°. The Grignard reagents of (II) and (III) with CO_2 yield 3-methoxydibenzfuran-4-, m.p. 156–157° (Me ester, m.p. 99.5–100°), and -2-carboxylic acid, m.p. 206–207° (Me ester, m.p. 122.5°), respectively. $p\text{-OMe-C}_6\text{H}_4\text{-OK}$ and 1:4:2- $\text{C}_6\text{H}_3\text{Br}_2\text{-NO}_2$ at 170° give 4-bromo-2-nitro-4'-methoxydiphenyl ether (crude), reduced by SnCl_2 to the amine, the diazonium chloride of which, when added to boiling 50% H_2SO_4 , yields 3-bromo-6-methoxydibenzfuran, m.p. 92.5° (debrominated by Pd-CaCO_3 to 3-methoxydibenzfuran). 4-Bromo-1-hydroxydibenzfuran (V) (prepared by Br-AcOH from the OH-compound), m.p. 151.5–152°, gives the Me ether, m.p. 97–97.5°, obtained in 86% yield from 1-methoxydibenzfuran by Br-AcOH and converted [method as for (II)] into 4-hydroxy-1-methoxydibenzfuran, m.p. 155°, which with HI and a little red P gives 1:4-dihydroxydibenzfuran, m.p. 217–218° (decomp.), and with Me_2SO_4 -NaOH gives 1:4-dimethoxydibenzfuran, m.p. 78.5°. 1-Aminodibenzfuran (prep. in 56.7% yield by a modified Hofmann reaction) and Ac_2O in C_6H_6 give the Ac derivative, which with Br-AcOH yields 4-bromo-1-acetamidodibenzfuran, m.p. 228°, and thence 4-bromo-1-aminodibenzfuran, m.p. 119–120°; the diazonium salt thereof with aq. CuSO_4 affords (V), and with HPO_2 gives 4-bromodibenzfuran (VI), m.p. 67°. Conc., aq. NH_3 and CuBr at 230–240° convert (VI) into 4-aminodibenzfuran, m.p. 74° (Ac derivative, m.p. 205°). By Grignard reactions (VI) affords 4-hydroxydibenzfuran, m.p. 140–140.5° (1- or 3-Br-derivative, m.p. 178°), and dibenzfuran-4-carboxylic acid, m.p. 232–233°, the Me ester, m.p. 63°, of which gives the 7-(?2-) NO_2 -ester, m.p. 216°, and thence a NO_2 -acid, m.p. 297–298°, decarboxylated by Cu bronze in quinoline to 2-nitrodibenzfuran. 1:4:2-

($\text{OMe})_2\text{C}_6\text{H}_3\text{-MgBr}$ and MgBu^nBr with O_2 give 43% of 2:5-dimethoxyphenol, b.p. 134–135°/15 mm. (benzoate, m.p. 73.5°), the K salt of which with $o\text{-C}_6\text{H}_4\text{Br-NO}_2$ at 170° yields 2-nitro-2':5'-dimethoxydiphenyl ether, b.p. 190–193°/3 mm., and thence (SnCl_2) the 2- NH_2 -ether, m.p. 72°, b.p. 183–185°/4 mm., which gives a phenol and not a dibenzfuran by diazotisation and treatment with H_2SO_4 .

XII. 1-Bromodibenzfuran and LiBu^n , first in Et_2O and then in C_6H_6 , give a Li derivative, converted by CO_2 into dibenzfuran-1-carboxylic acid (57.5% of pure acid), which is not obtained by the Grignard process. 3:7-Dibromodibenzfuran gives similarly up to 72% of the 3:7-dicarboxylic acid and some (?) dibutyldibenzfuran. 2-Bromodibenzfuran (VII) gives a 5:1 mixture of dibenzfuran-1- and -2-carboxylic acid; the 1-acid probably arises by reaction of Li 2-dibenzfuryl with (VII) to give Li 2-bromo-1-dibenzfuryl (and dibenzfuran), which then reacts with dibenzfuran to give Li 1-dibenzfuryl and regenerate (VII).

R. S. C.

Methylation of hydroxyflavanols. Quercetin, gossypetin, and herbacetin. P. S. RAO and T. R. SESHADRI (Current Sci., 1939, 8, 255–256).—Pentamethylquercetin, hexamethylgossypetin, m.p. 170–172°, and *O*-pentamethylherbacetin, m.p. 156–158°, are obtained exclusively and in good yield by methylation (Me_2SO_4 -NaOH- COMe_2) of the appropriate Ac derivative, using the method previously reported (A., 1939, II, 385).

F. N. W.

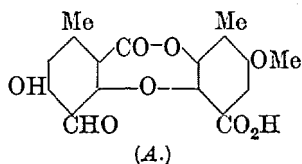
3-Hydroxyflavanone derivatives. I. New synthesis. Y. KIMURA (J. Pharm. Soc. Japan, 1939, 58, 123–127; cf. A., 1937, II, 70).—2-Hydroxy-4:6-dimethoxyacetophenone and 10% aq. NaOH-EtOH at 10–20°, with $p\text{-OMe-C}_6\text{H}_4\text{-CHO}$, 3:4:1-($\text{OMe})_2\text{C}_6\text{H}_3\text{-CHO}$, 3:4:5:1-($\text{OMe})_3\text{C}_6\text{H}_2\text{-CHO}$, or piperonaldehyde, respectively, afford 2-hydroxy-4:6:4'-trimethoxy-, m.p. 121°, -4:6:3':4'-tetramethoxy-, m.p. 117°, -4:6:3':4':5'-pentamethoxy-, m.p. 146°, and -4:6-dimethoxy-3':4'-methylenedioxyphenyl α -methoxystyryl ketone, m.p. 112–113°, converted by aq. HCl-EtOH into 3-hydroxy-5:7':4'-trimethoxy-, m.p. 158–159°, -5:7:3':4'-tetramethoxy-, m.p. 176°, -5:7:3':4':5'-pentamethoxy-, m.p. 168–169°, and -5:7-dimethoxy-3':4'-methylenedioxy-flavanone, m.p. 142°, respectively. A. T. P.

Pigments of the flavone series. V. Diosmin, a constituent of dahlia flowers. T. NAKAOI (J. Pharm. Soc. Japan, 1938, 58, 197–201).—The white flowers of *D. variabilis* contain apigenin (~2.5%), luteolin (~0.2%), and luteolin Me_1 ether rhamnoglucoside (I) (~0.5%). (I) is identical with diosmin (Oesterle *et al.*, A., 1925, i, 1438) and is shown to be 5:3'-dihydroxy-4'-methoxyflavone-7-rhamnoglucoside.

S. H. H.

Lichen substances. XCII. Psoromic acid. III. Y. ASAHINA and S. SHIBATA (Ber., 1939, 72, [B], 1399–1402).—Hypoparrellic acid Me_2 ether is transformed by SOCl_2 or conc. H_2SO_4 into 2:4:6-trimethoxy-3:5:8-trimethylxanthone (I), m.p. 187°, which does not react with CO; reagents under the usual conditions, has a blue fluorescence in Et_2O , gives a yellow solution in conc. H_2SO_4 which becomes

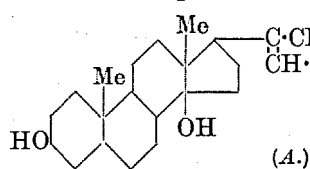
colourless when diluted with H_2O , and has an ultra-violet absorption spectrum resembling that of gentisein. It is a xanthone derivative since it is transformed by P_2S_5 and K_2S in xylene at 105–110° into 2:4:6-trimethoxy-3:5:8-trimethylxanthione, m.p. 159–5°, which is converted by NH_2OH , HCl and $NaOAc$ into 2:4:6-trimethoxy-3:5:8-trimethylxanthionoxime, m.p. 231° (decomp.). $NaNH_2$ and (I) in xylene at 150–180° afford 2':4:5-trimethoxy-3:6:3'-trimethyldiphenyl ether, m.p. 110°; identical with decarboxylated (I). Since energetic reduction of (I) gives deoxyhyposalazinol Me_3 ether, it is 2-carboxy-4:6:3'-trimethoxy-5:2':5'-trimethyldiphenyl ether, and psoromic acid is *A*. Hypoparcellic acid is converted by



conc. H_2SO_4 at room temp. into 4:6-dihydroxy-2-methoxy-3:5:8-trimethylxanthone, m.p. 319° (decomp.) after becoming discoloured at ~280°, whilst (I) with $Br-AcOH$ gives a *Br*-derivative, m.p. 264°, transformed by $SOCl_2$ into 7-bromo-2:4:6-trimethoxy-3:5:8-trimethylxanthone, m.p. 233°. H. W.

Isolation of xanthyletin from *Luvunga scandens*, Ham. E. SPÄTH, P. K. BOSE, E. DOBROVOLNY, and A. MOUKERJEE (Ber., 1939, 72, [B], 1450–1452).—Vac. sublimation of the coumarin fraction *G* obtained by Bose *et al.* from *L. scandens*, Ham, gives luvangetin and xanthyletin, m.p. 131–131.5°, identified by hydrogenation to tetrahydroxanthyletin, m.p. 158–159°. H. W.

Toad poisons. X. Constitution of bufalin. M. KOTAKE and K. KUWADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 36, 106–111; cf. A., 1934, 777).—The impure substance, m.p. 227°, obtained



after removal of cinobufagin and cinobufotalin is the acetate (I), m.p. 229–231°, of bufalin (*A*), $C_{24}H_{34}O_4$, m.p. 235–236°, which, with conc. HCl yields anhydrobufalin, m.p. 204.5–206° (acetate, m.p. 151–152°), and, in $AcOH$, with CrO_3 in aq. H_2SO_4 a ketone, $C_{24}H_{32}O_4$, m.p. 226–227°. With $Pd-H_2$, (I) in $EtOH$ gives tetrahydroacetylbufalin, m.p. 182–185°. W. McC.

Synthesis of diphenylene dioxide derivatives.

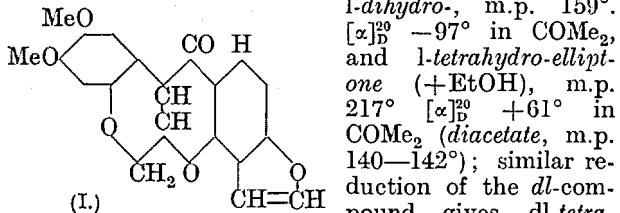
XIII. 2:6-Di-(α -hydroxy- γ -piperidinopropyl)-diphenylene dioxide. **XIV. β -Piperidinoalkyl-diphenylene dioxide.** M. TOMITA (J. Pharm. Soc. Japan, 1939, 58, 130–132, 133–136; cf. A., 1932, 1048).—XIII. 2:6-Diacetyldiphenylene dioxide and $(CH_2O)_2$ + piperidine hydrochloride in $C_5H_{11}OH$ (cf. Kamp *et al.*, A., 1936, 1390; Mannich *et al.*, A., 1922, i, 351; 1923, i, 43) afford 2:6-di-(β -piperidinopropionyl)diphenylene dioxide (I), m.p. 138° (hydrochloride, m.p. 231°). (I) and $Na-Hg$ in $EtOH$ give a N-free substance, m.p. >300°; catalytic reduction (PtO_2-EtOH at room temp.) of (I) gives 2:6-dipropionyl-, m.p. 241° (dioxime, m.p. 235°) [also obtained from diphenylene dioxide (II), $EtCOCl$, and $AlCl_3$], and 2:6-di-(α -hydroxy- γ -piperidinopropyl)-diphenylene

dioxide, m.p. 120°. (II), $Cl-[CH_2]_2-COCl$, and $AlCl_3$ give 2:6-di- β -chloropropionyldiphenylene dioxide, m.p. 211°, converted by piperidine into (I).

XIV. 2:6-Dimethyldiphenylene dioxide and $CH_2Cl-COCl-AlCl_3$ afford the 3:7-di(chloroacetyl) derivative, m.p. 248°, converted into the 3:7-di(piperidinoacetyl) compound, m.p. 163–165° (hydrochloride, +2 H_2O , m.p. >300°), and thence by $Na-Hg$ into 3:7-di-(α -hydroxy- β -piperidinoethyl)-2:6-dimethyldiphenylene dioxide, m.p. 211°. Similarly prepared are: [from (II)] 2:6-di-(α -bromopropionyl)-, m.p. 213°, -di-(α -piperidinopropionyl)-, m.p. 185–186°, and -di-(α -hydroxy- β -piperidinopropyl)-diphenylene dioxide, m.p. 215° (analysis not good); 2:6-di-(α -bromoisovaleryl)-, m.p. 196°, and -di-(α -piperidinoisovaleryl)-, m.p. 161° (some loss of piperidine); and -di-(α -bromoisobutyryl)-diphenylene dioxide, m.p. 160–167° (impure; loses Br on crystallisation). The last-named and piperidine give a substance, $C_{20}H_{16}O_4$, m.p. 255°. A. T. P.

Active principles of leguminous fish-poison plants. II. Isolation of l-elliptone from *Derris elliptica*. S. H. HARPER (J.C.S., 1939, 1099–1105).

—Quick extraction (5% KOH) of an ethereal extract of *D. elliptica* (var. Sarawak creeping) affords rotenone and l-elliptone (I), $C_{20}H_{16}O_6$, m.p. 160°, $[\alpha]_D^{20} +55^\circ$ in $COMe_2$, -18° in C_6H_6 (α -oxime, m.p. 222°; β -oxime, m.p. 236°; monoacetate, m.p. 200°). Racemisation of (I) with $NaOAc-EtOH$ gives dl-elliptone, m.p. 176–177°, $[\alpha]_D \pm 0^\circ$ in C_6H_6 (α -oxime, m.p. 259°; β -oxime, m.p. 261°; monoacetate, m.p. 202°), identical with Buckley's substance of m.p. 183° (B., 1936, 1117), of which (I) is the precursor. $NaOAc$ and I with (I) yield dehydroelliptone, m.p. 264°, $[\alpha]_D \pm 0^\circ$. Reduction of (I) with H_2-PtO_2 affords successively l-dihydro-, m.p. 159°.



$[\alpha]_D^{20} -97^\circ$ in $COMe_2$, and l-tetrahydro-elliptone (+ $EtOH$), m.p. 217° $[\alpha]_D^{20} +61^\circ$ in $COMe_2$ (diacetate, m.p. 140–142°); similar reduction of the dl-compound gives dl-tetrahydroelliptone (+ $EtOH$), m.p. 205°. From a study of its reactions and by comparison with those of isorotenone, structure (I) is suggested. F. R. S.

Thiophen derivatives from ethyl β -carbethoxy-lævulate. S. MITRA, N. K. CHAKRABARTY, and S. K. MITRA (J.C.S., 1939, 1116–1117).— $Et \beta$ -carbethoxylævulate dissolved in the appropriate alcohol, saturated with HCl , with H_2S gives the *Me*, b.p. 125°/5 mm., *Et*, b.p. 150°/5 mm., and *Pr^a* ether, b.p. 135°/5 mm., of *Et* 5-hydroxy-2-methylthiophen-3-carboxylate. These are hydrolysed to 5-methoxy-, m.p. 128°, -ethoxy-, m.p. 122° (*Ba* salt), and -*n*-propoxy-2-methylthiophen-3-carboxylic acid, m.p. 75°, dealkylated to the 5-OH-acid (I), m.p. 160°. These acids condense with aromatic aldehydes ($EtOH-HCl$) to form dithienylarylmethanes: di-(5-ethoxy-3-carboxy-2-methyl-4-thienyl)-phenylmethane, m.p. 233°, and -4'-hydroxy-3'-methoxyphenylmethane, m.p. 235°, and di-(5-*n*-propoxy-, m.p. 232° (decomp.), and di-(5-methoxy-3-carboxy-2-methyl-4-thienyl)phenylmethane, m.p. 250°

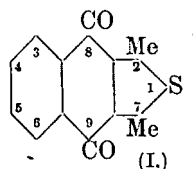
(decomp.). Condensation of (I) with aldehydes gives yellow dyes: 5-keto-4-benzylidene-, m.p. 166°, -4-o-nitrobenzylidene-, m.p. 184° (decomp.), -4-o-methoxybenzylidene-, m.p. 152°, -4-ethylidene-, m.p. 124°, and -4-cinnamylidene-2-methyl-4:5-dihydrothiophen-3-carboxylic acid, m.p. 204°.

F. R. S.

Thiophen series. XLV. 5-Hydroxy-2-methylthiophen (thiotenol). W. STEINKOPF and F. THORMANN (Annalen, 1939, 540, 1—7).—5-Hydroxy-2-methylthiophen (I) (prepared by distilling $\text{COMe} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ and P_2S_5 in CO_2), m.p. -23.5° to 22.5°, b.p. 94—96°/15 mm., gives a benzoate, m.p. 47—47.5°, and the known acetate, but condenses as a ketone with aldehydes. With PhCHO and HCl in abs. EtOH at room temp., it gives 57% of 5-keto-4-benzylidene-2-methyl-4:5-dihydrothiophen, m.p. 85—86°. Cryst. FeCl_3 in boiling EtOH gives bis-3-keto-2-methyl-4:5-dihydro-4-thienylidene ["bis-(2-methylthiophen)-4-indigo"], m.p. 188—190°, sublimes at 14 mm. With acenaphthenequinone and HCl - AcOH at 100°, it gives 7-keto-8-5'-keto-2'-methyl-4':5'-dihydro-4'-thienylidene-7:8-dihydroacenaphthene [acenaphthene-(1)-2-methylthiophen-(4)-indigo], m.p. 164°. With 3:4-dibromothiophen-2:5-dialdehyde (II) in HCl - AcOH at 100°, it gives 3:4-dibromo-2:5-di-(5'-keto-2'-methyl-4':5'-dihydro-4'-thienylidenemethyl)thiophen [3:4-dibromo-2:5-thioxylydenebis-3'-(5'-keto-2'-methyl-4':5'-dihydrothiophen)], m.p. 232—234°. 3:4-Dibromo-2:5-di-(2'-keto-1':2'-dihydro-1'-thionaphthenylidenemethyl)thiophen [3:4-dibromo-2:5-thioxylydenebis-1'-(2'-keto-1':2'-dihydrothionaphthen)], cryst., is obtained from (II) and 2-hydroxythionaphthen in boiling HCl - AcOH . With $p\text{-C}_6\text{H}_4(\text{CHO})_2$ in boiling HCl - AcOH , (I) gives xylylidenebis-4'-(5'-keto-2'-methyl-4':5'-dihydrothiophen), $o\text{-C}_6\text{H}_4(\text{CH}:\text{C} < \begin{smallmatrix} \text{CH}:\text{CMe} \\ \text{CO-S} \end{smallmatrix})_2$, m.p. 167—168°, and very little 5-keto-4-p-aldehydobenzylidene-2-methylthiophen, m.p. 277—279°. The $\text{C}_4\text{H}_3\text{S}$ is strongly bathochromic compared with Ph .

R. S. C.

Thiophen series. XLVI. Derivatives of 2:5-thioxen [2:5-dimethylthiophen]. W. STEINKOPF, T. BARLAG, and H. J. VON PETERSDORFF (Annalen, 1939, 540, 7—14).—2:5-Dimethylthiophen, $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 at 0—5° give 62% of 3-o-carboxybenzoyl-2:5-dimethylthiophen, m.p. 127—128° (*Et* ester, b.p. 152—153°/high vac.), does not give an amide; 4-*Br*-derivative, m.p. 186°, reduced by Zn in boiling AcOH - H_2O (4:1) to α -2:5-dimethyl-3-thienylphthalide (64%), m.p. 154°, and cyclised, best (18%) by AlCl_3 - NaCl at 140°, to 2:5-dimethylnaphtha-1':4'-quinonyl-2:3'-3:4-thiophen [2:7-dimethyl- β -thionaphthanthrenequinone] (I), m.p. 175—176°. 3-Iodo-2:5-dimethylthiophen and Cu -bronze at 245—250° give di-2:5-dimethyl-3-thienyl, b.p. 142—144°/9 mm., purified by conversion into the 4:4'-diacetoxymercuri-derivative, m.p. 233—234°, and regeneration therefrom by 18% HCl at 100°. 5-Acetyl-2-methyl- or 3-acetyl-2:5-dimethylthiophen with isatin and KOH in aq. EtOH at 110° yield 2-2'-methyl-5'-, m.p. 227—228° (*Me* ester, m.p. 91—92°, b.p. 176—178°/high vac.), and 2-2':5'-

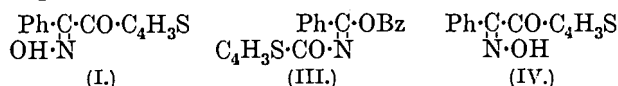


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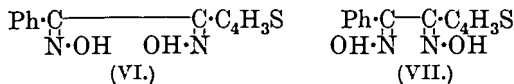
dimethyl-3'-thienylquinoline-4-carboxylic acid, m.p. 214—215° (*Me* ester, m.p. 79—80°), decarboxylated by soda-lime at ~360° to 2-2'-methyl-5'-, m.p. 122—123° (*picrate*, m.p. 192—194°), and 2-2':5'-dimethyl-3'-thienylquinoline, an oil, respectively. 2-2'-Thienylquinoline, m.p. 132—133° (*picrate*, m.p. 194—195°), is similarly obtained from the 4-carboxylic acid.

R. S. C.

Thiophen series. XLVII. Phenyl 2-thienyl diketone and its oximes. W. STEINKOPF and, in part, G. BOKOR (Annalen, 1939, 540, 14—24).—Addition of $\text{C}_5\text{H}_{11}\text{O}\cdot\text{NO}$ to CH_2Ph 2-thienyl ketone and NaOEt in EtOH at <0° gives *Ph* 2-thienyl diketone *Bz*-syn-mono-oxime (I), m.p. 88°, the benzoate, m.p. 111—113°, of which is converted by hot, dil.



NaOH - EtOH into PhCN and thiophen-2-carboxylic acid (II) and is thus (III). H_2SO_4 - EtOH rapidly or HCl - AcOH - Ac_2O slowly converts (I) at room temp. into PhCN and (II). Boiling, conc. H_2SO_4 (short treatment) or HCl - EtOH at room temp. converts (I) into the *Bz*-anti-mono-oxime (IV), m.p. 144°, the benzoate, m.p. 139—140°, of which regenerates (IV) with alkali and is thus the normal benzoate. Hot, conc. H_2SO_4 hydrolyses (I) or (IV) into *Ph* 2-thienyl diketone (V), m.p. 65—65.5°, which is yellow when melted and thereafter when cooled in Et_2O - CO_2 , but becomes colourless again when recrystallised. When (I) is treated with NaOEt - EtOH and benzoin, the reaction, $(\text{OK}\cdot\text{CPh})_2 + (\text{V}) \rightarrow \text{OK}\cdot\text{CPh}\cdot\text{COPh} + \text{OK}\cdot\text{CPh}\cdot\text{CO}\cdot\text{C}_4\text{H}_3\text{S}$ [or $\text{COPh}\cdot\text{C}(\text{OK})\cdot\text{C}_4\text{H}_3\text{S}$], occurs, since subsequent oxidation gives (V) (47.6), Bz_2 (52.4), BzOH (77.64), and (II) (22.36%). With $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ at 125°, (V) gives 2-phenyl-3-2'-thienylquinoxaline, m.p. 128°. With NH_2OH , HCl and aq. NaOH , (I) gives *Ph* 2-thienyl anti-diketoxime (VI), m.p. variable, 193—195° (*diacetate*, m.p. 173.5—175.5°), and some syn-diketoxime (VII), m.p. 173—175° [*diacetate*, m.p. 165—166° after sintering; obtained also from (VI) by NH_2OH , HCl and aq. NaOH or by conc. HCl at 60—65°]; hydrolysis of the diacetates regenerates the



original dioximes. 2-Cyanothiophen, m.p. 51.5°, is obtained in ~70% yield from 2- ω -oximinoacetylthiophen by AcCl at 0° (less well by Ac_2O) and converted by conc. HCl into 2-thienylglyoxylic acid (80% yield), m.p. (+ H_2O) 52—53°, (anhyd.) 91.5°. Passage of CH_2O into Mg 2-thienyl iodide in Et_2O (apparatus described) gives 66% of 2-hydroxymethylthiophen, b.p. 94.5—96°/12 mm.

R. S. C.

Synthesis of thianthren (diphenylene disulphide) derivatives. Friedel-Crafts reaction with thianthren. Synthesis of 2:8-di-(α -hydroxy- β -piperidinoethyl)thianthren. M. TOMITA (J. Pharm. Soc. Japan, 1939, 58, 139—141; cf. A., 1939, II, 442).—Thianthren (I) (Friedel-Crafts) affords 2:8-di(chloroacetyl)- (II), m.p. 177°, and thence -di(piperidinoacetyl)-, m.p. 129° (hydrochloride, m.p. 260°), and

2 : 8-di-(α -hydroxy- β -piperidinoethyl)-thianthren, m.p. 208°. (I) and AcCl-AlCl_3 give 2 : 8-diacetylthianthren, m.p. 157°, oxidised [as is (II) also] by $\text{CrO}_3\text{-AcOH}$ to diphenylenedisulphone-2 : 8-dicarboxylic acid, m.p. >300°, obtained also by similar oxidation of 2 : 6-dimethylthianthren, m.p. 126°. A. T. P.

Phenoxthionine and thianthren derivatives. II. **Synthesis of phenoxthionine and thianthren oxide derivatives.** M. TOMITA and T. IKEDA (J. Pharm. Soc. Japan, 1938, 58, 231—232).—Phenoxthionine 10-oxide or 10 : 10-dioxide or thianthren 9 : 9 : 10 : 10-tetraoxide does not undergo the Friedel-Crafts reaction with $\text{CH}_2\text{Cl-COCl}$. H_2O_2 converts 2 : 8-dichloroacetylphenoxthionine into the 10 : 10-dioxide, m.p. 224—229°, and 2 : 6-dichloroacetylthianthren into the 9 : 9 : 10 : 10-tetraoxide, m.p. 209—213°. With piperidine, these products give N- and Cl-free substances of high m.p., stated to be polymerised vinyl ketones. R. S. C.

Synthesis of phenoxthionine derivatives. I. **Friedel-Crafts reaction with phenoxthionine.** **Synthesis of 2 : 8-di-(α -hydroxy- β -piperidinoethyl)phenoxthionine.** M. TOMITA (J. Pharm. Soc. Japan, 1939, 58, 136—139).—Phenoxthionine and $\text{CH}_2\text{Cl-COCl-AlCl}_3$ afford 2 : 8-di(chloroacetyl)- (I), m.p. 193°, and thence, with piperidine, 2 : 8-di(piperidinoacetyl)-, m.p. 105°, and (Na-Hg) 2 : 8-di-(α -hydroxy- β -piperidinoethyl)-phenoxthionine, m.p. 133°. (I) and Zn-Hg give 2 : 8-diethylphenoxthionine (II), m.p. 205—206°, also obtained from the 2 : 8- Ac_2 derivative (III), m.p. 175° (prepared by Friedel-Crafts reaction), similarly. $(4\text{-C}_6\text{H}_4\text{Ac})_2\text{O}$ similarly affords 4 : 4'-diethylbiphenyl ether, b.p. 161—163°, converted by S-AlCl_3 into (II). (II) is oxidised (CrO_3) to 2 : 8-diethylphenoxthionine 10-dioxide (IV), m.p. >300° (Me_2 ester, m.p. 204—208°). $(4\text{-C}_6\text{H}_4\text{Me})_2\text{O}$, S, and AlCl_3 afford 2 : 8-dimethylphenoxthionine, m.p. 73—74° (cf. Hilditch *et al.*, J.C.S., 1911, 99, 408), oxidised (CrO_3) to (IV). A. T. P.

Oximinopyrroles. XI. **Transformation products of 3-oximino-2 : 5-dimethylpyrrole.** T. AJELLO and S. CUSMANO (Gazzetta, 1939, 69, 207—214).—2 : 5-Dimethylpyrrole (new prep. from $\text{COMe}[\text{CH}_2]_2\text{COMe}$ and NH_4OAc in boiling AcOH , followed by treatment with aq. NH_3 and extraction with Et_2O) with NaOEt-EtOH and $\text{C}_5\text{H}_{11}\text{O-NO}$ gives the Na salt (I) of 3-oximino-2 : 5-dimethylpyrrole. When (I) is acidified and the product steam-distilled or extracted with Et_2O , 3-acetyl-5-methylisoxazole (cf. Angelico and Calvillo, A., 1904, i, 443; Schmidt and Widmann, A., 1909, i, 525) [oxime, m.p. 117° (Bz derivative, m.p. 180°); semicarbazone, m.p. 238—239°; azine, m.p. 156—158°] is formed. E. W. W.

Studies in the pyrrole series. I. **Synthesis of certain N-alkyl-substituted 2 : 5-dimethylpyrrole-3(4)-carboxylic acid esters.** N. M. TIMOSHEVSKAJA (J. Gen. Chem. Russ., 1939, 9, 406—408).— $\text{CH}_3\text{Ac-CHAc-CO}_2\text{Et}$ and NH_2R in EtOH yield Et 1 : 2 : 5-trimethyl-, 2 : 5-dimethyl-1-ethyl-, m.p. 25—26°, 1-n-propyl-, b.p. 144°/4 mm., m.p. 44—5°, and 1-n-butyl-pyrrole-3-carboxylate, b.p. 162—163°/4 mm. R. T.

Imidoporphyrins. VI. **2-Methyl-3 : 4-diethyl- and 3 : 4-diethyl-pyrrole.** Curtius degradation of Et 2-methyl-3 : 4-diethylpyrrole-5-carboxylate. H. FISCHER, H. GUDEMOS, and A. SCHÄFER (Annalen, 1939, 540, 30—50; cf. A., 1939, II, 288).—Numerous pyrrole, pyrromethene, and imidoporphyrin derivatives are synthesised. 3-Acetyl-5-benzeneazo-, m.p. 143° (hydrochloride, m.p. 134°), and 5-p-sulphobenzeneazo-2-methyl-4-ethylpyrrole, decomp. 222°, prepared by coupling, do not give the 5-amino-pyrrole when hydrogenated (PtO_2). $\text{N}_3\text{H}_4\text{-NaOEt-EtOH}$ converts 3-acetyl-2-methyl-4-ethylpyrrole into 2-methyl-3 : 4-diethylpyrrole (I), b.p. 104—106°/11 mm., and some 1-amino-2-methyl-3 : 4-diethylpyrrole, m.p. 68°, b.p. 140°/11 mm. (picrate, m.p. 170°); $\text{H}_2\text{-Raney Ni}$ at 180°/200 atm. gives 70% of (I) and some of a substance, b.p. 76—77°/11 mm. (picrate, m.p. 115°). $\text{H}_2\text{-Raney Ni}$ similarly reduces Et 3-acetyl-2-methyl-4-ethylpyrrole-5-carboxylate to Et 2-methyl-3 : 4-diethylpyrrole-5-carboxylate (II) (42%), m.p. 75°, obtained also with some Et 2-methyl-3 : 4-diethylpyrrole-1-carboxylate, an oil [readily converted into (I)], from (I) by ClCO_2Et . Photo-oxidation of (I) in Et_2O gives an oil, from which H_2O_2 yields 2-hydroxy-3 : 4-diethylpyrrole-5-carboxylic acid, m.p. 124°. SO_2Cl_2 (3 mols.) and (II) give an oily Cl_3 -derivative, hydrolysed by boiling H_2O to 2-carbethoxy-3 : 4-diethylpyrrole-5-carboxylic acid, decomp. 264°, which with 10% NaOH at 160° yields 3 : 4-diethylpyrrole, b.p. 83°/10 mm. [PhN_2 -derivative, decomp. 222° (picrate, decomp. 182°); gives no picrate or 2-CHO derivative], unstable in air. $\text{N}_3\text{H}_4\text{, H}_2\text{O}$ and (II) at 150° give the hydrazide, m.p. 163° (obtained similarly from the 1- CO_2Et -derivative), which with NaNO_2 in AcOH at 0—5° yields 2-methyl-3 : 4-diethylpyrrole-5-carboxylazide (III), decomp. 98°. 1 mol. of SO_2Cl_2 in Et_2O converts (III) into an unstable Cl_3 -derivative, which with MeOH at 35° gives 2-methoxymethyl-3 : 4-diethylpyrrole-5-carboxylazide, decomp. 58°. 2 mols. of SO_2Cl_2 in Et_2O yield 2-dichloromethyl-3 : 4-diethylpyrrole-5-carboxylazide, decomp. 97°, converted by MeOH containing a little H_2O into 2-formyl-3 : 4-diethylpyrrole-5-carboxylazide, decomp. 68°, and by $\text{CH}_2\text{Ph-OH}$ in boiling xylene into N-2-formyl-3 : 4-diethyl-5-pyrrolyl-O-benzylurethane, decomp. 205° (azine, m.p. 198°). 3 mols. of SO_2Cl_2 with (III) in Et_2O gives an oily Cl_3 -derivative, which reacts violently with MeOH to give N-2-carbomethoxy-3 : 4-diethyl-5-pyrrolyl-O-methylurethane, m.p. 113°. Boiling MeOH or $\text{CH}_2\text{Ph-OH}$ in boiling xylene converts (III) into urethanes, (IV) $\text{C}_{11}\text{H}_{18}\text{O}_3\text{N}_2$, decomp. 119°, and $\text{C}_{17}\text{H}_{22}\text{O}_3\text{N}_2$, decomp. 136°, respectively, which are probably auto-oxidation products, give no picrates, and yield oils with $\text{H}_2\text{-Pd-black}$. In 50% AcOH at 100° (III) gives N_2 and 5-amino-2-methyl-3 : 4-diethylpyrrole, an unstable oil (picrate, m.p. 182°); 5-amino-2 : 4-dimethyl-3-ethylpyrrole [5-aminocryptopyrrole] (picrate, m.p. 201°; picrolonate, darkens at 200°, decomp. 224°) is analogously obtained; it cannot be diazotised or acylated. A hygroscopic by-product obtained in the treatment of Et 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with $\text{N}_3\text{H}_4\text{-NaOEt}$ (A., 1929, 1463) has m.p. 60° and is 1-aminocryptopyrrole. The 1- NH_2 -derivatives obtained in such reactions are formed by ring-fission of the pyrroles to diketones, followed by

condensation thereof with N_2H_4 . Et 2-bromomethyl-3:4-diethylpyrrole-5-carboxylate (improved prep.), decomp. 120—121°, in a little boiling MeOH gives Et_2 3:4:3':4'-tetraethylpyrromethene-5:5'-dicarboxylate, m.p. 98°, converted by boiling 50% KOH into a dicarboxylic acid, which with Br-AcOH affords 5:5'-dibromo-3:4:3':4'-tetraethylpyrromethene, m.p. 163° (hydrobromide). With NH_3 -EtOH at 140°, this gives octaethyl- $\beta\delta$ - (or $\alpha\gamma$ -)di-imidodorphyrin (V), m.p. 291° (absorption max. at 6232 and 5411 Å.; removed from Et_2O by 20% HCl), which is also obtained with a little octaethyl- $\alpha\gamma$ - ($\beta\delta$ -)di-imidodorphyrin (absorption max. 6132, 5580, and 5326 Å.; removed from Et_2O by 11% HCl) from (IV) and $NHPh-NH_2$ at 180—240°. With $AgOAc$ or $KOAc$ in boiling AcOH or, much less well, with $NaOMe$ at 160—165°, 5-bromo-5'-methyl-3:4:3':4'-tetraethylpyrromethene hydrobromide gives 5-hydroxy-5'-methyl-3:4:3':4'-tetraethylpyrromethene, m.p. 230°, converted by Br-AcOH into a violet, cryst. product, $C_{35}H_{46}O_3N_4$. 3-Bromo-2-formyl-4-methyl-5-pyrrolyl-*O*-ethylurethane and cryptopyrrole in hot $HBr-H_2O-MeOH$ yield 3-bromo-4:3':5'-trimethyl-4'-ethylpyrromethene-5-ethylurethane, decomp. 154—155°. 2-Formyl-4-methyl-3-ethyl-5-pyrrolyl-*O*-ethylurethane with cryptopyrrole in aq. $HBr-AcOH$ or opsonic acid in aq. $HBr-HCO_2H$ gives 4:3':5'-trimethyl-3:4'-diethylpyrromethene-5-*O*-benzylurethane, m.p. 140° (unstable hydrobromide), and CH_2Ph 4:3'-dimethyl-3-ethylpyrromethene-5-carbaminate-4'-propionic acid hydrobromide, m.p. 203—204°, respectively. R. S. C.

Reactions with amyl nitrite. II. T. AJELLO (Gazzetta, 1939, 69, 315—322).—2:3:5-Triphenylpyrrole with $C_5H_{11}O\cdot NO$ (I) in Et_2O gives 4-nitro-2:3:5-triphenylpyrrole (II), m.p. 192—194°, reduced (Al in 30% KOH) to the 4- NH_2 -compound, to which the *Me ether*, m.p. 195°, of (II) is also reduced by $Zn-AcOH$. 2:5-Diphenylpyrrole and (I) give a substance, $C_{16}H_{12}O_3N_2$ (?), m.p. 300°, and 3-nitro-2:5-diphenylpyrrole (III), m.p. 174°, reduced as above to the NH_2 -compound, to which the *Me ether* is also reduced. With (I), oximino-di- and -tri-phenylpyrrole give (II) and (III), respectively. E. W. W.

Local anaesthetics from β -2-piperidylethyl alcohol. L. A. WALTER and R. J. FOSBINDER (J. Amer. Chem. Soc., 1939, 61, 1713—1714).—2- β -Hydroxyethylpiperidine hydrochloride and the appropriate acid chloride (1 mol.) in hot, dry $CHCl_3$ give β -2-piperidylethyl benzoate, m.p. 189—191° (lit., 182—183°), *p*-, m.p. 209—210°, *m*-, m.p. 170—172°, and *o*-nitro-, m.p. 148—150°, *p*-, m.p. 249—251°, *m*-, m.p. 177—180°, and *o*-amino-, m.p. 209—211°, *p*-ethoxy-, m.p. 146—148°, 3-nitro-, m.p. 150—155° and 3-amino-4-ethoxy-benzoate, m.p. 173—175°, and cinnamate, m.p. 180—182°. The *N*-phenylurethane has m.p. 200—202°. A few pharmacological data are given. 2- β -Hydroxyethylpiperidine is best (15—20%) obtained from α -picoline (I) and 40% CH_2O (2 parts by wt.) at 120°, followed by $Na-EtOH$. Li picolinyl with $(CH_2)_2O$ or $MeCHO$ gives 40% of 2- γ -hydroxy-*n*- and 2- α -hydroxyiso-propylpyridine, readily reduced to the piperidinyl alcohols. M.p. are corr. R. S. C.

Catalytic transformations of heterocyclic compounds. XII. Conversion of tetrahydropyran into piperidine, *N*-ethylpiperidine, and tetrahydrothiopyran. J. K. JURIEV, E. J. PERVOVA, and V. A. SAZONOVA. **XIII.** Synthesis of pyrrolidine and thiophan by catalytic dehydration of butane- $\alpha\delta$ -diol in presence of ammonia or hydrogen sulphide. J. K. JURIEV and N. G. MEDOVSCHTSCHIKOV (J. Gen. Chem. Russ., 1939, 9, 590—594, 628—630).—XII. Tetrahydropyran passed in a stream of NH_3 over Al_2O_3 at 360—430° gives piperidine (I) in 20% yield; *N*-ethylpiperidine is prepared analogously, with NH_2Et , and tetrahydrothiopyran (II) with H_2S . (I) and H_2S at 415° (Al_2O_3 catalyst) yield (II).

XIII. $(OH\cdot CH_2\cdot CH_2)_2$ and NH_3 or H_2S at 400° similarly give pyrrolidine (35% yield) or thiophan (63% yield). R. T.

Hydrogenation of hydroxy-amides. J. D. D'ANNI and H. ADKINS (J. Amer. Chem. Soc., 1939, 61, 1675—1681).—Hydrogenation of α -, γ -, δ -, and ϵ -OH-amides gives mainly NH_2 -alcohols, better in presence of Cu chromite at 250—260° than of Raney Ni at 225°. β -OH-amides are reduced and dehydrated. More complex cases are also studied. Lactopiperidide, b.p. 128—129°/7 mm., with H_2-Cu chromite and H_2-Ni , respectively, gives β -piperidinopropyl alcohol (51, 27%), $\alpha\beta$ -dipiperidinopropane (10, 0%) (picrate, m.p. 171—172°), $OH\cdot CHMe\cdot CH_2\cdot OH$ (10, 18%), piperidine (I) (10, 38%), and 1-*n*-propylpiperidine (4, 0%). β -Hydroxybutyropiperidide (prep. from the Et ester at 200°, b.p. 118—123°/7 mm., with H_2-Cu chromite gives 1-*n*-butylpiperidine (78) and (I) (12%), but with H_2-Ni gives *n*-butyropiperidide (86%), b.p. 105—109°/7 mm., and (I) (12%). γ -Hydroxy-*n*-valeropiperidide with H_2-Cu chromite or $-Ni$, respectively, gives ϵ -piperidinopentan- β -ol (79, 15%), b.p. 107°/6 mm. (picrate, m.p. 97—98°), $\alpha\delta$ -dipiperidino-*n*-pentane (6, 0%), b.p. 118—119°/1 mm. (dipicrate, m.p. 168—169°), (I) (7, 44%), and γ -valerolactone (0, 58%). δ -Hydroxy-*n*-hexopiperidide, b.p. 135—140°/1 mm., with H_2-Cu chromite or $-Ni$, respectively, gives ζ -piperidino-*n*-hexan- β -ol (76, 34%), b.p. 123—125°/7 mm. (picrate, m.p. 86—89°), $\alpha\epsilon$ -dipiperidino-*n*-hexane (6, 0%), b.p. 122—123°/0.5 mm. (dipicrate, m.p. 166—167°), (I) (4, 29%), and δ -hexolactone (0, 15%). ϵ -Hydroxy-*n*-heptopiperidide, b.p. 145—148°/0.5 mm., with H_2-Cu chromite gives η -piperidino-*n*-heptan- β -ol (60%), b.p. 105—106°/1 mm. (picrate, m.p. 62—64°), $\alpha\zeta$ -dipiperidino-*n*-heptane (14%), b.p. 127—130°/1 mm. [dipicrate, m.p. 203—205° (decomp.)], heptane- $\alpha\zeta$ -diol (26%), and (I) (9%). *n*-Hexopiperidide is largely unchanged by H_2 -Raney Ni, giving *n*- $C_6H_{13}\cdot OH$ (5), (I) (7), and 1-*n*-hexylpiperidine (6%). *NN*-Di-*n*-amylmalonamide, b.p. 146°, with H_2-Cu chromite gives 1-*n*-amylpyrrolidone (32), $NH(C_5H_{11})_2$ (30), succin-*n*-amylimide (14), *NN*-di-*n*-amylsuccinamide (12), b.p. 180—181°, 1-*n*-amylpyrrolidine (II) (9), and $NH_2\cdot C_5H_{11}\cdot n$ (7%); *NN*-di-*n*-amyltartaramide, b.p. 194—195°, gives $NH(C_5H_{11}\cdot n)_2$ (20), (II) (11), and $NH_2\cdot C_5H_{11}\cdot n$ (8%); 5-phenyl-2:4-dimethyl-4-oxazolidone gives mandelamide (35), $OH\cdot CHPh\cdot CH_2\cdot OH$ (29), $CH_2Ph\cdot CH_2\cdot OH$ (3), and $NHPr_2$ (47%). *Muco*-

dipiperidide (344 g.), b.p. 231° (decomp.), with H_2 -Cu chromite at 250° (less well at 225–235° or with Raney Ni at 175–200°) suffers fission only between $C_{(8)}$ and $C_{(9)}$, giving (I) (23), 1-ethyl- (10), 1-*n*-butyl- (7.5), 1- β -hydroxyethyl- (7), 1-acetyl- (4.2), and ζ -hydroxy-*n*-hexyl-piperidine (11.5), $\alpha\beta$ -dipiperidinoethane (12), $\alpha\delta$ -dipiperidino-*n*-butane (44) (*dipicrate*, m.p. 185–186°), $\alpha\zeta$ -dipiperidino-*n*-hexane (12.5), $\alpha\zeta$ -dipiperidino-*n*-hexan- β -ol (22), b.p. 125–130°/1 mm. (*dipicrate*, m.p. 138–139°; *dihydrochloride*, m.p. 189–191°), $\alpha\zeta$ -dipiperidino-*n*-hexane- β -diol (16), b.p. 150–160°/1 mm. (*dipicrate*, m.p. 170–173°), and adipdipiperidide (11 g.). Boiling (I) with $OH\cdot CMe_2\cdot CH_2\cdot CO_2Et$ or $OH\cdot CMe_2\cdot CO_2Et$ gives mainly β - β' -hydroxybutyroxylbutyropiperidide, b.p. 105–110°/1 mm., and α - α' -hydroxyisobutyroxylisobutyropiperidide, b.p. 108–108.5°/1 mm., respectively.

R. S. C.

1-Azadicyclo-[1 : 3 : 3]-nonane. V. PRELOG, S. HEIMBACH, and R. SEIWERTH (Ber., 1939, 72, [B], 1319–1325).— $CH_2(CO_2Et)_2$, NaOEt, and $OPh\cdot[CH_2]_3\cdot Br$ in boiling EtOH afford Et_2 γ -phenoxypropylmalonate, b.p. 207–208°/7 mm., converted by prolonged boiling with $OPh\cdot[CH_2]_3\cdot Br$ and NaOEt in EtOH into Et_2 di- γ -phenoxypropylmalonate, b.p. 245–250°/0.01 mm., m.p. 42–43.5°; the corresponding acid, m.p. 123–123.5°, is decarboxylated at 180–200° to $\alpha\eta$ -diphenoxyheptane- δ -carboxylic acid, m.p. 65°, the *Et* ester, b.p. 248°/0.05 mm., of which is reduced by Na-abs. EtOH to $\alpha\eta$ -diphenoxy- δ -hydroxymethylheptane, b.p. 255°/0.3 mm.; this with 68% HBr at 100° gives $\alpha\eta$ -dibromo- δ -bromomethylheptane, b.p. 170–175°/0.03 mm., which does not yield a *tert.* base when heated with NH_3 -MeOH. *Et* nicotinoylacetate hydrochloride is reduced (PtO_2 according to Bruce in EtOH) to *Et* β -3-piperidylpropionate (I), b.p. 141–142°/10 mm. (yield 33.5% varying greatly with quality of catalyst). 3- β -Piperidylpropionic acid hydrochloride has m.p. 229°. Na and boiling EtOH reduce (I) to γ -3-piperidylpropanol, b.p. 154°/10 mm., whence 3- γ -bromopropylpiperidine hydrobromide, m.p. 154°, transformed by 0.1*N*-NaOH at 50° into 1-azadicyclo-[1 : 3 : 3]-nonane (II), b.p. ~175°, m.p. 114° (hydrochloride, volatilises without melting at >350°; platinichloride, m.p. 226°; picrate, m.p. 283°; picrolonate, m.p. 231°; methiodide, m.p. 351°). *Et* $\alpha\eta$ -diethoxyheptane- δ -carboxylate, b.p. 166–168°/22 mm., is reduced by Na and abs. EtOH to $\alpha\eta$ -diethoxy- δ -hydroxymethylheptane, b.p. 158–161°/15 mm., converted by PBr_3 and C_2H_5N into $\alpha\eta$ -diethoxy- δ -bromomethylheptane, b.p. 153°/11 mm. This with KCN in EtOH- H_2O gives $\alpha\eta$ -diethoxy- δ -cyanomethylheptane, b.p. 171–172°/12 mm., hydrolysed to ϵ -ethoxy- α - γ' -ethoxypropylhexoic acid, b.p. 206°/12 mm., which is converted through the azide into $\alpha\eta$ -diethoxy- δ -aminomethylheptane, b.p. 150–151°/10 mm. The corresponding hydrobromide and 67% HBr at 100° afford $\alpha\eta$ -dibromo- δ -aminomethylheptane hydrobromide, m.p. 159°, converted by 0.1*N*-NaOH at 50° into (II) in 79% yield. All m.p. are corr.

H. W.

Hydrogenations in the pyridine series. P. KARRER (Annalen, 1939, 539, 297–298).—Concerning priority (cf. Mumm *et al.*, A., 1939, II, 339). R. S. C.

Polarisation in heterocyclic rings with aromatic character. E. OCHIAI (J. Pharm. Soc. Japan, 1939, 59, 20–28).—Examination of the literature of heterocyclic compounds from the electronic viewpoint shows that, as with isocyclic compounds, the chemistry of heterocyclic compounds can be divided into rings of alicyclic and aromatic character. The heterocyclic rings of alicyclic type can be considered in accordance with that of aliphatic derivatives and those of aromatic character can be treated in the same manner as C_6H_6 derivatives if the following hypotheses are accepted. The development of aromatic character in heterocyclic rings is due to the presence of six-membered rings with three conjugated double linkings or of five-membered rings which contain at least one hetero-atom (O, S, Se) or radical (NH) with a lone pair of electrons and two double linkings. Gradual differences are observed in the intensity of the aromatic character of aromatic heterocyclic rings. The most important underlying factor is the polar effect of the hetero-atoms, particularly of those with a lone pair of electrons. The chemical reaction of the heterocyclic ring of aromatic character is greatly influenced by the polar effect of the hetero-atoms of the rings. Substituents which are present exert their polar effect. It is therefore possible that the substitution of hetero-rings which are devoid of substituents occurs in the same manner as the reaction of substitution products of C_6H_6 which are similarly polarised. Thus pyrrole and $PhOH$, C_5H_5N and $PhNO_2$ have many properties in common. These four hypotheses are in good agreement with the behaviour of compounds with one ring and one hetero-atom. Detailed consideration is given to polarisation in the furan, thiophen, and pyrrole rings and in the C_5H_5N ring. H. W.

Pyrid-2-one-5-sulphonamide and certain derivatives. C. NAEGELI, W. KÜNDIG, and H. BRANDENBURGER (Helv. Chim. Acta, 1939, 22, 912–924).—2-Chloropyridine-5-sulphonamide is converted by 10% NaOH at 110° into pyrid-2-one-5-sulphonamide, m.p. 269–271°, in 88% yield, which is not increased by the addition of Cu powder or $CuSO_4$; aq. Na_2CO_3 or $NaHCO_3$ is without action. 2-Chloropyridine-5-sulphonyl chloride and 33% NH_4Me in $COMe_2$ afford 2-chloropyridine-5-sulphonmethylamide, m.p. 111–112°, transformed by boiling 10% NaOH containing Cu powder into pyrid-2-one-5-sulphonmethylamide, m.p. 188–190°. The following are analogously obtained: 2-chloropyridine-, m.p. 115–117°, and pyrid-2-one-, m.p. 212–214°, -5-sulphondimethylamide; 2-chloropyridine-, m.p. 86–87°, and pyrid-2-one-, m.p. 163.5–165°, -5-sulphon-diethylamide; 2-chloropyridine-, m.p. 78°, and pyrid-2-one-, m.p. 159–160°, -5-sulphonallylamide; 2-chloropyridine-, m.p. 90–92°, and pyrid-2-one-, m.p. 178°, -5-sulphon-*n*-butylamide; pyrid-2-one-5-sulphonanilide, m.p. 214–215°; 2-chloropyridine-, m.p. 116–118°, and pyrid-2-one-, m.p. 169–172°, -5-sulphoncyclohexylamide; 2-chloropyridine-, m.p. 131–132°, and pyrid-2-one-, m.p. 236–238°, -sulphonpiperidide; pyrid-2-one-5-sulphonmorpholide, m.p. 262–264°; 2-chloropyridine-, m.p. 197°, and pyrid-2-one-, m.p. 282°, -5-sulphon-*p*-nitroanilide, pyrid-2-one-5-sulphon-*p'*-aminoanilide, m.p. 246°; N^4 -pyrid-2'-one-5'-, m.p. 250–252°, N' -2'-pyridyl-

*N*⁴-2'-chloropyridine-5'-, m.p. 266°, and *N*'-2''-pyridyl-*N*⁴-pyrid-2'-one-5'-sulphonyl-5'-, m.p. 301—302°, -sulphonylsulphanilamide; 2-(pyrid-2'-one-5'-sulphonamido)pyridine-5-sulphonamide, m.p. 295° (incipient decomp.); 2-2'-Chloropyridine-5'-sulphonamidopyridine, m.p. 235—236°, and 2-(*NN*-di-2'-chloropyridine-5'-sulphon)amidopyridine, m.p. 197—199°, are described. 2-2'-Ethoxypyridine-5'-sulphonamidopyridine and 2-butoxypyridine-5-sulphonallyl-amine have m.p. 180° and 67—68°, respectively.

H. W.

Indoline aldehydes.—See B., 1939, 809.

Synthesis of nitrogen ring compounds. XII. Synthesis of quinoline derivatives. II. Synthesis of 6 : 7-dimethoxyquinoline. S. SUGASAWA, K. KAKEMI, and T. TSUDA (J. Pharm. Soc. Japan, 1938, 58, 80—82).—3 : 4 : 1-(OMe)₂C₆H₃·[CH₂]₂·CO₂H with HNO₃-AcOH at 40—50° gives 6-nitro-3 : 4-dimethoxyhydrocinnamic acid, m.p. 188°, reduced catalytically in EtOH at 2 atm. to 6 : 7-dimethoxyhydrocarbostyryl (I), m.p. 136° (not obtained by action of HN₃ on 5 : 6-dimethoxyhydrindone), identified by its prep. by reduction of 6-nitro-3 : 4-dimethoxycinnamic acid. With P₂S₅ and K₂S in xylene at 90—95°, (I) gives 6 : 7-dimethoxyhydrothiocarbostyryl, m.p. 151°, reduced electrolytically in 20% EtOH-H₂SO₄ (Pb anode; 1 amp. per sq. cm.; 25—35°) to 6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroquinoline (hydrochloride, m.p. 196°; NO-derivative, m.p. 137°; Bz derivative, m.p. 102°). This is dehydrogenated (method : Hoshino and Takiura, A., 1936, 863) to 6 : 7-dimethoxyquinoline [hydrochloride, m.p. 232° (decomp.), picrate, m.p. 251—252° (decomp.)].

E. W. W.

[Attempted] Ullmann reaction with nitrogenous heterocyclic compounds. M. TOMITA and H. WATANABE (J. Pharm. Soc. Japan, 1938, 58, 223—230).—Condensation of 7-hydroxy-6-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (I) with 8-bromo-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (II) by KOMe and Cu catalysts, first at 180° and then at 220°, failed, giving unchanged (I) and, by debromination of (II), the Me ether of (I). 3 : 4 : 1-OMe·C₆H₃(O·CH₂Ph)·CH·CH·NO₂ [prep. in 75% yield from 3 : 4 : 1-OMe·C₆H₃(O·CH₂Ph)·CHO and MeNO₂ by NH₂Me, HCl and Na₂CO₃ at room temp.], m.p. 123—124°, is reduced electrolytically to 3 : 4 : 1-OMe·C₆H₃(O·CH₂Ph)·[CH₂]₂·NH₂, the hygroscopic formate, m.p. 146—149° (decomp.), of which at 180—200°/vac. yields the *N*-CHO derivative, m.p. 57—63°. With POCl₃ in hot PhMe this gives 7-benzoyloxy-6-methoxy-3 : 4-dihydroisoquinoline (24%), m.p. 183° (and 7-hydroxy-6-methoxy-3 : 4-dihydroisoquinoline, m.p. 182°), which affords the methiodide, m.p. 194°, and thence the hygroscopic methochloride, which, best, with H₂-PtO₂ in H₂O gives (I), m.p. 167°. 5-Bromo-ω-nitro-3 : 4-dimethoxystyrene, m.p. 159°, is obtained from 3 : 4 : 5 : 1-(OMe)₂C₆H₃Br·CHO [prep. from 4 : 3 : 5 : 1-OH·C₆H₃Br(OMe)·CHO by Me₂SO₄-NaOH], MeNO₂, and KOH-aq. EtOH, and by the methods given above yields β-5-bromo-3 : 4-dimethoxyphenylethylamine (formate, hygroscopic; *N*-CHO derivative, an oil), 8-bromo-6 : 7-dimethoxy-3 : 4-dihydroisoquinoline, m.p. 102° [hydrochloride, decomp.

E E* (A., II.)

196°; methiodide, m.p. 179° (decomp.); methochloride, hygroscopic, and (II), an oil [platinichloride, m.p. 213° (decomp.); hydrochloride, hygroscopic, m.p. 210°]. The structure of (II) is proved by its prep. from (I) by Br-AcOH (gives the 8-Br-derivative, m.p. 185°), followed by CH₂N₂.

R. S. C.

Amyostatic poisons. Synthesis of polyamino-hydrocarbostyryls. U. UEDA (Proc. Imp. Acad. Tokyo, 1939, 15, 148—155).—The structure of the derivatives described below is proved by the oxidations noted. Nitro- and particularly polynitro-hydrocarbostyryls suffer ring-fission by 0.5*N*-NaOH and the resulting acids can be isolated. Aminohydrocarbostyryls are usually too unstable to be isolated except as salts. Colour reactions with Br-H₂O distinguish 3-NH₂- and 3 : 6-(NH₂)₂- from 3 : 8-(NH₂)₂- and 3 : 6 : 8-(NH₂)₃-derivatives. Hydrocarbostyryl (I) with H₂SO₄-HNO₃ (*d* 1.52) at 0° gives the 6-NO₂-derivative (II), m.p. 203—204° [oxidised by KMnO₄ to 5 : 2 : 1-NO₂·C₆H₃(NH₂)·CO₂H], converted by further nitration into the 6 : 8-(NO₂)₂-derivative (III), m.p. 177°, also obtained directly from (I) (cf. Menon *et al.*, A., 1930, 795). Zn-HCl at 100° reduces (II) to 6-aminohydrocarbostyryl, m.p. 178° (hydrochloride, decomp. ~315°; Bz, m.p. 241°, and Ac derivative, m.p. 263—264°). With 0.05*N*-KOH at 100°, (III) gives β-3 : 5-dinitro-2-aminophenylpropionic acid, but with hot *N*-NaOH gives 2 : 3 : 5 : 1-OH·C₆H₂(NO₂)₂·[CH₂]₂·CO₂H, m.p. 159—160°. Zn-HCl and (III) give 6 : 8-diaminohydrocarbostyryl (Bz₂ derivative, m.p. 264—265°). H₂SO₄-HNO₃ (*d* 1.52) at 100° oxidises as well as nitrates (I), giving 3 : 6 : 8-trinitrocarbostyryl (IV), m.p. 182° (cf. Kaufmann, A., 1917, i, 354). 6 : 8-Dinitro-3-acetamidohydrocarbostyryl (V) (prep. from the 3-NHAc-compound), m.p. 235°, and K₂Cr₂O₇ in hot 30% H₂SO₄ give 2 : 3 : 5 : 1-NH₂·C₆H₂(NO₂)₂·CO₂H and thence by NaOH 2 : 3 : 5 : 1-OH·C₆H₂(NO₂)₂·CO₂H. Hot 0.05*N*-NaOH converts (V) into α-acetamido-β-3 : 5-dinitro-2-aminophenylpropionic acid, m.p. 225° (decomp.), and Zn-HCl yields 3 : 6 : 8-triaminohydrocarbostyryl [hydrochloride; Bz₃ derivative, m.p. 250°, obtained also from (IV) by red P and HI (*d* 1.7) and subsequent benzylation, whence the structure of (IV) follows].

R. S. C.

Sharp-tasting acylamines. T. SZÉKI (Math. nat. Anz. ung. Akad. Wiss., 1936, 54, 807—818; Chem. Zentr., 1937, i, 1690; cf. A., 1930, 597).—Piperoylpyrrolidine, m.p. 144°, which is analogous in constitution to piperine, has a sharp taste. The aminophenol group in the spicy acylamines may be replaced by an NH₂-alcohol; thus NH₂·[CH₂]₃·OH gives spicy derivatives (piperoyl-, m.p. 148.5°, producing a strong burning action on the mucous membrane; undecenoyl-, m.p. 53°, similar in odour to capsaicine). Piperoyl-β-aminoethanol, m.p. 162°, has no spicy character, but the undecenoyl derivative, m.p. 70.5°, has a sharp, aromatic taste. Substitution of C₆H₃·O₂CH₂ or C₆H₃(OMe)₂ in the C-chain of the NH₂·[CH₂]₃·OH grouping (β-undecenamido-α-hydroxydihydroisosafole, m.p. 95°, and -dihydroisoeugenol Me ether, m.p. 91°) destroys the spicy taste. Compounds of unsaturated acids with piperidine and pyrrolidine (undecenoyl-, b.p. 170°/3 mm. and 168°/3 mm., re-

spectively) are spicy. *Undecenoyl-4-aminoquinoline*, m.p. 71.5° (*hydrochloride*, m.p. 169°), *tetrahydroquinoline*, b.p. 234—235°/4 mm., *piperoyl-4-aminoquinoline*, m.p. 233°, *tetrahydroquinoline*, m.p. 145°, and *diundecenoylpiperazine*, m.p. 63°, are tasteless. The prep. of the above compounds from the base and piperoyl or undecenoyl chloride is described.

A. J. E. W.

Constitution of the quinaldinic acids. V. M. MITCHOVITCH (Bull. Soc. chim., 1939, [v], 6, 1156—1162).— Me_3 quinaldine-3 : 4-dicarboxylate (A., 1938, II, 293) and excess of PhCHO at 160—165° afford the *CHPh* derivative, m.p. 124°, hydrolysed by KOH-EtOH to 2-styrylquinoline-3 : 4-dicarboxylic acid (I), $+\text{H}_2\text{O}$, m.p. 213° [= m.p. of (II)]. It loses $2\text{H}_2\text{O}$ at 100—110°/0.2 mm. to give the *anhydride* (II), m.p. 213°, convertible into (I). (I) and KMnO_4 -aq. KOH at 100° (bath) give *quinoline 2 : 3 : 4-tricarboxylic acid*, $+\text{H}_2\text{O}$, m.p. 254° (decomp.) (Me_3 ester, m.p. 102.5°). Isatic acid and $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ afford *quinoline-3-acetic acid-2 : 4-dicarboxylic acid*, m.p. 245° (decomp.) [Et_2 ester, m.p. 195° (decomp.)].

A. T. P.

Quinoline series. IV. New synthesis of quinic acid. E. THIELEPAPE and A. FULDES (Ber., 1939, 72, [B], 1432—1443).—Acet-*N*-methyl-*p*-methoxyacetanilide is converted by $\text{Et}_2\text{C}_2\text{O}_4$ and NaOEt in Et_2O into *ethoxalylacet-N-methyl-p-methoxyacetanilide*, m.p. 80.0—80.5° (corr.) [Cu salt, m.p. 194—195° (corr.)], converted by conc. H_2SO_4 at $<-5^\circ$ into *Et 2-keto-6-methoxy-1-methyl-1 : 2-dihydroquinoline-4-carboxylate* (I), m.p. 105° (corr.), which is hydrolysed by aq. NaOH to the acid, m.p. 316—317° (corr.) [Me ester, m.p. 113° (corr.)]. Addition of (I) to a boiling solution of PCl_5 in POCl_3 affords *Et 2-chloro-6-methoxyquinoline-4-carboxylate* (II), m.p. 100° (corr.), hydrolysed by boiling very dil. NaOH to 2-chloro-6-methoxyquinoline-4-carboxylic acid (III), m.p. 230° (corr.; decomp.). Boiling 30% NaOH transforms (II) into 2-hydroxy-6-methoxyquinoline-4-carboxylic acid, m.p. 335—336° (corr.) [Me , m.p. 233—234° (corr.), and Et , m.p. 195° (corr.), ester]. Red P, KI, and HI (*d* 1.5 or 1.7) transform (II) at 100° and subsequently at 150° into 2-iodo-6-methoxyquinoline-4-carboxylic acid (IV), m.p. 190° (corr.; decomp.) after becoming brown at 186° (corr.). (II) is transformed by SnCl_2 and HCl (*d* 1.19) at 100° into 6-methoxyquinoline-4-carboxylic (quinic acid), m.p. 285° (corr.; decomp.) [hydrazide, m.p. 154° (corr.); aurichloride, m.p. 223° (corr.); stannichloride, $(\text{C}_{11}\text{H}_9\text{O}_3\text{N}_2\text{HCl})_2\text{SnCl}_4$, m.p. 274—275° (corr.; decomp.); picrate, m.p. 244° (corr.); Et , m.p. 69° (corr.), and Me , m.p. 87° (corr.), ester]. Dechlorination of (II) or (III) could not be effected in presence of Pt-sponge, whereas Pd-BaSO_4 is almost quantitatively efficient at room temp. Dehalogenation of (IV) occurs slowly in presence of Pt-sponge. H. W.

Course of the quinoline synthesis with tetrahydronaphthylamines. 7 : 8-Tetramethylenequinoline. J. LINDNER and B. ZAUNBAUER (Monatsh., 1939, 72, 213—215).—1-Aminotetrahydronaphthylamine, glycerol, H_2SO_4 , and PhNO_2 afford 7 : 8-tetramethylenequinoline, m.p. 26° [*hydrochloride*, m.p. ~215° (decomp.); picrate, m.p. 186°]. H. W.

Hydrindene derivatives. III. 7 : 8-Trimethylenequinoline and -quinaldine. J. LINDNER, J. SELLNER, and A. BERGER. IV. 5 : 6- and 6 : 7-Trimethylenequinoline. J. LINDNER, J. SELLNER, E. HOFMANN, and J. HAGER. V. 5 : 6- and 6 : 7-Trimethylenequinaldine. J. LINDNER, A. BERGER, and W. MIGNON. VI. Action of formaldehyde on, and proof of the constitution of, 6 : 7-trimethylenequinaldine. J. LINDNER and J. HAGER (Monatsh., 1939, 72, 330—334, 335—349, 354—360, 361—367).—III. 4-Aminohydrindene with glycerol, conc. H_2SO_4 , and PhNO_2 gives 7 : 8-trimethylenequinoline, m.p. 51—53° [*hydrochloride*, decomp. ~210°; *hydrobromide*, decomp. ~210°; *hydriodide*, decomp. >210°; picrate, m.p. 211—212° (decomp. from ~207°)], and with MeCHO , HCl , and H_2SO_4 at 100° gives 2-methyl-7 : 8-trimethylenequinoline, m.p. 89° (*hydrochloride*, decomp. 250°; *hydrobromide*, decomp. ~230°; *hydriodide*, decomp. ~240—250°; picrate, m.p. 190—191°).

IV. 5-Aminohydrindene (I) gives >90% of 6 : 7-(II), m.p. 79—80.5° [*hydrochloride*; *hydrobromide*; *hydriodide*; picrate, m.p. 269—271° (decomp.)], and <10% of 5 : 6-trimethylenequinoline (III), m.p. 43—44.5° (*hydrochloride*; *hydrobromide*; *hydriodide*; picrate, m.p. 190—191°). KMnO_4 converts (II) into *quinoline-6 : 7-dicarboxylic acid*, m.p. 240—250° (decomp. from 230°) (Me_3 ester, m.p. 104.5°). (III) gives the known *quinoline-5 : 6-dicarboxylic acid*, m.p. 228° (lit., 238—241°) (Me_3 ester, sinters at 119°, m.p. 120—121°).

V. By the Döbner-Miller quinaldine synthesis, (II) gives 2-methyl-6 : 7- (IV), m.p. 93—95° (*hydrochloride*; *hydrobromide*, decomp. ~185°; *hydriodide*, decomp. ~190—195°; picrate, m.p. 202—203°), with a very small amount of -5 : 6-trimethylenequinoline (V), m.p. 53—54° (picrate, m.p. 193—194°).

VI. The constitution of (IV) and thus by exclusion of (V) is proved as follows. 70% of (IV) is recovered after heating with 40% aq. CH_2O (0.85 mol.) at 100°, but the remainder yields 6 : 7-trimethylene-2- β -hydroxyethyl- (VI), m.p. 92—93°, -2- $\beta\beta'$ -dihydroxyisopropyl-, m.p. 121—122°, and -2- $\beta\beta\beta'$ -tri-hydroxy-tert.-butylquinoline, m.p. 165°. With HI (*d* 1.96) and red P at 100°, (VI) gives 6 : 7-trimethylene-2- β -iodoethylquinoline, an oil [*hydriodide*, m.p. 124° (sinters at 120°; decomp. from 100°)], converted by conc. $\text{NaOH-H}_2\text{O-COME}_2$ into 6 : 7-trimethylene-2-vinylquinoline, m.p. 65°, which with $\text{KMnO}_4\text{-H}_2\text{SO}_4$ at 0° gives 6 : 7-trimethylenequinoline-2-carboxylic acid, decomp. ~208—210°. This, when heated with Ba(OH)_2 in N_2 at 220—230°/vac., gives (II).

The above reactions show that the ethylenic linkings of hydrindene exist mostly, but not entirely, as in $\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}_2 > \text{CH}_2$.

R. S. C.

Heterocyclic derivatives of *p*-aminobenzene-sulphonamide and 4 : 4'-diaminodiphenylsulphone. W. H. GRAY (J.C.S., 1939, 1202).—*p*-Aminobenzene-sulphonamide with 2-chloropyridine (I) gives *p*-(2-pyridylamino)-, m.p. 235°, and with 2-chloroquinoline (II) affords *p*-(2-quinolylamino)-benzenesulphonamide, m.p. 263° (*hydrochloride*, m.p. 279°). *pp'*-Diaminodiphenylsulphone with (I) yields *pp'*-bis-(2-pyridylamino)-, m.p. 241°, and with (II) gives

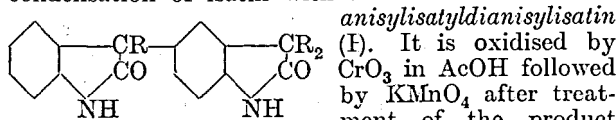
-(2-quinolylamino)-diphenylsulphone, m.p. 306°. These compounds have low toxicity but are inactive in streptococcal and pneumococcal infections of mice.

F. R. S.

10-Substituted acridoneanils and acridoneazines. K. GLEU and R. SCHAARSCHMIDT (Ber., 1939, 72, [B], 1404—1407).—The additive compound (I) of 10-methylacridine and POCl_3 is almost instantaneously converted by NH_2Ph in cold H_2O into 10-methylacridoneanil, m.p. 162°. 10-Ethyl-, m.p. 147°, and 10-phenyl-, m.p. 142°, -acridoneanil are obtained similarly. Under analogous conditions (I) and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ afford 10-methylacridoneazine, m.p. 290°; the hydrazone is not obtained even with a very large excess of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. 10-Ethyl-, m.p. 204°, and 10-phenyl-, m.p. 286°, -acridoneazine are described.

H. W.

Diphenylisatin and its derivatives. III. By-products of dianisylisatin and their oxidation products. IV. Monobromo-compounds of dianisylisatin and their oxidation products. V. Oxidation product of diacetoxyphephenylisatin. VI. Ditolyisatin and its oxidation products. VII. Synthetic preparation of phenyldioxindoles and their oxidation products. S. INAGAKI (J. Pharm. Soc. Japan, 1939, 59, 1—4, 4—5, 5—6, 7, 7—10).—III. The by-product, m.p. 325—327°, of the condensation of isatin with anisole is identified as



(I.) $\text{R} = \text{C}_6\text{H}_4 \cdot \text{OMe}-p$ with conc. H_2SO_4 to $\text{CO}(\text{C}_6\text{H}_4 \cdot \text{OMe}-p)_2$ and $p\text{-OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$. With MeI it yields a Me_2 compound and is acetylated to a diacetate. Bromination of dianisylisatin (II) gives a 5-bromodianisylisatin. Oxidation with CrO_3 in AcOH causes union of 1 O with each isatin nucleus and acetylation of 1 NH, giving a compound, decomp. 178—180°; this when treated successively with conc. H_2SO_4 , H_2O , and NaOH gives *o*-amino-*p*'-methoxybenzhydrylanhydro-2-acetamido-4':4''-dimethoxytriphenylcarbinol or anhydro-*o*-acetamido-*p*'-methoxybenzhydryl-2-amino-4':4''-dimethoxytriphenylcarbinol, m.p. 203—204°. Isatin is converted by Mg *o*-methoxyphenyl iodide into *o*-methoxyphenylisatylcarbinol, m.p. 240°; this with anisole and conc. H_2SO_4 yields 3-2':4''-dimethoxydiphenylisatin, m.p. 232° (*Ac* derivative, m.p. 172°), which is not identical with (I); it is oxidised and then converted by H_2SO_4 , H_2O , and NaOH into 2'-amino-2'':4'''-dimethoxytriphenylcarbinol.

IV. 4-, 5-, 6-, and 7-Bromoisatin have been prepared and the position of Br therein has been determined by oxidation by H_2O_2 to the corresponding bromoanthranilic acids. They condense with anisole in AcOH containing conc. H_2SO_4 to 4-, m.p. 211°, 5-, m.p. 220°, 6-, m.p. 193—194°, and 7-, m.p. 222—224°, bromodianisylisatin, of which the 5-derivative is identical with the product of the bromination of (II) in AcOH . These are oxidised by CrO_3 in AcOH to 4-, m.p. 213—214°, 5-, m.p. 220°, 6-, m.p. 201—202°, and 7-, m.p. 198—199°, bromodianisylisatoic anhydride, respectively. The anhydrides lose CO_2

when treated with conc. H_2SO_4 and the products are transformed by H_2O and NaOH into 3-, non-cryst., 4-, m.p. 125—128°, 5-, m.p. 143—145°, and 6-, m.p. 235—236°, -bromo-2-amino-4':4''-dimethoxytriphenylcarbinol. 3-Bromo-2-acetamido-4':4''-dimethoxytriphenylcarbinol has m.p. 149—152°.

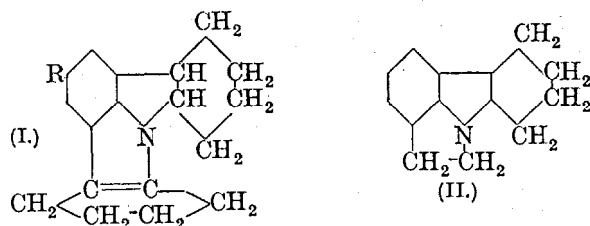
V. Oxidation of 3-4':4''-diacetoxyphephenylisatin with CrO_3 in AcOH gives a small yield of diacetoxyphephenylisatoic anhydride, which is transformed by conc. H_2SO_4 into 2-amino-4':4''-dihydroxytriphenylmethane (III), m.p. 218° (*Ac*₃ derivative, m.p. 139°), and 2-hydroxy-5-4'-hydroxyphenylacridine (IV), m.p. >350° (diacetate, m.p. 167°). 2-Amino-4':4''-dimethoxytriphenylcarbinol is transformed by Zn and AcOH into 2-acetamido-4':4''-dimethoxytriphenylmethane, which is converted by $\text{HBr} \cdot \text{AcOH}$ into (III). NH_2Ph and $m\text{-C}_6\text{H}_4(\text{OH})_2$ afford 3-hydroxytriphenylamine, which is condensed with $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ in presence of ZnCl_2 to (IV).

VI. Condensation of isatin with PhMe by conc. H_2SO_4 gives 3-*p*'*p*'-ditolyisatin, m.p. 204—205°, oxidised by CrO_3 in AcOH to ditolyisatoic anhydride, which with conc. H_2SO_4 loses CO_2 and gives 2-amino-4':4''-dimethyltriphenylcarbinol.

VII. The action of the requisite Grignard reagent on powdered isatin gives *p*-, m.p. 205°, *m*-, m.p. 200°, and *o*-, m.p. 215—216°, -tolyldioxindole and *p*-, m.p. 194°, *m*-, m.p. 179.5°, and *o*-, m.p. 240°, -anisylloxindole. All are colourless. Conc. H_2SO_4 gives red colours with the *p*- and *m*- but blue colours with the *o*-compounds. They are converted by Ac_2O at 145° or by boiling Ac_2O containing NaOAc into the *Ac*₂ derivatives, m.p. 158°, 136°, 142—144°, 143°, 133—134°, and 160°, respectively. Phenyldioxindole yields a diacetate, m.p. 143°. Oxidation of the oxindoles by H_2O_2 in alkaline solution affords respectively *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO}_2\text{H}$ and *o*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me}-p$; *m*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO}_2\text{H}$ and 2-amino-3'-methylbenzophenone, m.p. 60°; *o*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{CO}_2\text{H}$ and 2-amino-2'-methylbenzophenone, m.p. 81—82°; *p*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ and *o*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}-m$; *m*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ and 2-amino-3'-methoxybenzophenone; *o*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ and 2-amino-2'-methoxybenzophenone, m.p. 110°.

H. W.

Stereochemistry of tervalent nitrogen. F. LIONS and E. RITCHIE (J. Amer. Chem. Soc., 1939, 61, 1927—1928).—Manjunath's "8:9-(1':2'-cyclohexyl)tetrahydrocarbazole" (A., 1927, 978) was really (I) ($\text{R} = \text{H}$). 9-Nitroso-6-methyl-1:2:3:4:1a:4a-hexahydrocarbazole, cyclohexanone, and Zn dust in AcOH give similarly the substance (I)



($\text{R} = \text{Me}$), but no analogue could be obtained from the 8-methylcarbazole derivative owing to steric hindrance. A similar reaction with 1-nitrosoindoline gives the substance (II), m.p. 154°.

R. S. C.

Formation and constitution of skatole-red from urine. M. RANGIER and P. DE TRAVERSE (Compt. rend., 1938, 207, 1257—1259; cf. A., 1939, III, 393).—Urochrome, freed from indoxyl sulphate and glucuronates, with 2% H_2SO_4 at 100° affords indoxyl, removed by Et_2O . Evaporation of the mother-liquor yields a substance, m.p. 85° , which polymerises easily, gives a red colour [skatole-red (I)] with warm HCl in air, and with FeCl_3 an intense blue. (I) is probably indirubin. J. L. D.

Amino-acids. XI. Condensation of creatinine with aromatic aldehydes. P. CATTANEO, V. DEULOFEU, and T. H. GUERRERO (Ber., 1939, 72, [B], 1461—1470).—5-*p*-Hydroxybenzylidenecreatinine, m.p. 284—285 or, + Ac_2O , m.p. 225—227°, obtained from creatinine and *p*-OH· C_6H_4 ·CHO at 150 — 155° or in boiling piperidine (Ac derivative, m.p. 225°), is reduced by Na—Hg in H_2O to 5-*p*-hydroxybenzylcreatinine, m.p. (dry) 255— 256° . The following -creatinines are obtained analogously: 5-3'-hydroxy-4'-methoxy-benzylidene-, m.p. 280° , and -benzyl-, m.p. 253° ; 5-2':4'-dimethoxy-benzylidene-, m.p. 244 — 245° (2-Ac derivative, m.p. 205°), and -benzyl- (Ac derivative, m.p. 129°); 5-3':4'-dimethoxybenzylidene-, m.p. 244 — 245° (Ac derivative, m.p. 213 — 214°); 5-3':4':5'-trimethoxy-benzylidene-, m.p. 257 — 258° (2-Ac derivative, m.p. 215°), and -benzyl- (2-Ac derivative, m.p. 125°); 5-furfurylidene-, m.p. 273 — 275° (2-Ac derivative, m.p. 252°), and 5-furfuryl- (2-Ac derivative, m.p. 189°); 5-cinnamylidene-, m.p. 280° (2-Ac derivative, m.p. 248°); 2-acetyl-5-2'-acetoxy-3'-methoxybenzylidene-, m.p. 218° ; 5-*o*-methoxybenzylidene-, m.p. 243 — 244° (2-Ac derivative, m.p. 194°), and *o*-methoxybenzylidene- N^2N^2 -di-5-*o*-methoxybenzylidene-, new m.p. 306 — 308° ; 5-*m*-methoxybenzylidene-, m.p. 231° , 5-*m*-methoxybenzyl-, m.p. 268° (non-cryst. 2-Ac derivative), and *m*-methoxybenzylidene- N^2N^2 -di-5-*m*-methoxybenzylidene-, m.p. 270° ; 5-*p*-methoxybenzylidene-, m.p. 259° , and *p*-methoxybenzylidene- N^2N^2 -di-5-*p*-methoxybenzylidene-, prisms or needles, m.p. $>300^\circ$; 3-4-dimethoxybenzylidene- N^2N^2 -di-5-3:4-dimethoxybenzylidene-, m.p. 260° ; 5-4'-hydroxy-3':5'-dimethoxybenzylidene-, m.p. 250° or, + AcOH , m.p. 148° (Ac₂ derivative, m.p. 205°), and 4-hydroxy-3:5-dimethoxybenzylidene- N^2N^2 -di-5-4-hydroxy-3:5-dimethoxybenzylidene-, m.p. $>300^\circ$ (Ac₂ derivative, m.p. $>300^\circ$); *o*-chlorobenzylidene-, new m.p. 250 — 251° (2-Ac derivative, m.p. 193°), 2-acetyl-5-*o*-chlorobenzyl-, m.p. 148° , and *o*-chlorobenzylidene- N^2N^2 -di-5-*o*-chlorobenzylidene-, m.p. 274 — 275° ; 2-acetyl-5-*m*-chlorobenzylidene-, m.p. 178° , hydrolysed by boiling 2*N*-HCl to 5-*m*-chlorobenzylidene-, m.p. 265° , 2-acetyl-5-*m*-chlorobenzyl-, m.p. 160° , and *m*-chlorobenzylidene- N^2N^2 -di-5-*m*-chlorobenzylidene-, m.p. 300° ; 5-*p*-methylbenzylidene-, new m.p. 270 — 271° (2-Ac derivative), 5-*p*-methylbenzyl-, m.p. 270 — 282° (2-Ac derivative, m.p. 175°), and *p*-methylbenzylidene- N^2N^2 -di-5-*p*-methylbenzylidene-, m.p. 309° ; benzylidene- N^2N^2 -di-5-benzylidene-, m.p. 281 — 282° or, in individual cases, 292° . H. W.

Reaction between organic sulphur compounds and hydrogen peroxide. XII. Constitution of antipyrine and related compounds. I. R. KITAMURA (J. Pharm. Soc. Japan, 1938, 58, 86—101;

cf. A., 1938, II, 206).—Thiopyrine (I) with aq. KOH and H_2O_2 slowly gives antipyrine (II). 3-Thiopyrine (III) also slowly gives 3-antipyrine (IV), and antithiopyrine and bithiopyrine (V) give bisantipyrine (VI). $\text{MeCS}\cdot\text{NPhMe}$ and 1-phenyl-3:4:4-trimethyl-5-thiopyrazole (VII) react more rapidly, as do

$$\begin{array}{c} \text{CMe}-\text{CH} \\ | \\ \text{NMe}-\text{S}-\text{C} \\ | \\ \text{NPh} \end{array} \quad \begin{array}{l} \text{HCS}\cdot\text{NPh}, \text{ PhCS}\cdot\text{NH}_2, \text{ PhCS}\cdot\text{NPh}, \\ \text{and MeCS}\cdot\text{NPh}. \end{array}$$

(I) may be due to tautomerism between a preponderant but little reactive betaine form (A) and a more reactive form

$\begin{array}{c} \text{CH}-\text{CS} \\ | \\ \text{CMe}\cdot\text{NMe} \end{array} \text{NPh (B) (Knorr's formula). Neutral } \text{H}_2\text{O}_2 \text{ converts (I) into thioantipyrine trioxide, decomp. } 301\text{—}302^\circ \text{ (new temp.)}, \text{ but does not react with (VII). The stability of (II), (IV), pyrimidone (VIII), and 4-aminoantipyrine (IX) to Pt—Pd—H}_2 \text{ is against formula (B). Coloured compounds with FeCl}_3 \text{ are described, as follows. From (I), (II), (IV), and (IX), compounds of type } 3\text{M}, 2\text{FeCl}_3, \text{ decomp. } 115\text{—}120^\circ, 220\text{—}300^\circ, 180\text{—}187^\circ, \text{ and } 243\text{—}245^\circ, \text{ respectively; from (V), (VI) and methylenebisantipyrine, compounds of type } 3\text{M}, 4\text{FeCl}_3, \text{ decomp. } 169\text{—}172^\circ, 250\text{—}260^\circ, \text{ and } 174\text{—}179^\circ, \text{ respectively; and from (VIII) a compound, M, FeCl}_3, \text{ decomp. } 132\text{—}134^\circ. \text{ All these compounds support formula (A); relations between colour and constitution of antipyrines etc. are discussed. Absorption spectra indicate the co-existence of both structures; abnormalities of m.p. are against formula (B). When melted, (I) and (III) become yellow, and 3-selenopyrine yellowish-brown; loss of colour on cooling suggests a } (A) \rightleftharpoons (B) \text{ tautomerism. Selenopyrine is, however, yellow in both cryst. and melted states. While (II) distils unchanged at } 147^\circ/0.05 \text{ mm., supporting formula (B), (I) at } \sim 140^\circ/0.05 \text{ mm. in part distils unchanged, and in part gives } \psi\text{-thiopyrine. It is concluded that the structure of (I) is best represented by forms (B) and } \begin{array}{c} \text{CH}-\text{CS} \\ | \\ \text{CMe}\cdot\text{N}^+\cdot\text{Me} \end{array} \text{NPh in equilibrium, and of (II) by similar forms in which O replaces S. E. W. W.}$

Reaction between organic sulphur compounds and hydrogen peroxide. XIII. Constitution of antipyrine and related compounds. II. Proof of the betaine form. R. KITAMURA (J. Pharm. Soc. Japan, 1938, 58, 161—164).—Thiopyrine trioxide

(I), $\begin{array}{c} \text{NMe}\cdot\text{NPh} \\ | \\ \text{CMe}-\text{CH} \end{array} \text{C}\cdot\text{SO}_3$ (from thiopyrine and neutral H_2O_2), is unaffected by cold aq. KOH but with H_2O_2 and KOH in 60% EtOH at room temp. for 36 hr. gives antipyrine (II), thus establishing the betaine structure of (II). Conversion of (I) into (II) is also effected with 0.5*N*-KOH at 100° (bath) and, less readily, *N*- K_2CO_3 ; hot *N*-HCl is without action. H. B.

Reaction between organic sulphur compounds and hydrogen peroxide. XIX. Mechanisms of reaction. XX. Constitution of antipyrine and related compounds: tautomerism and mesomerism. R. KITAMURA (J. Pharm. Soc. Japan, 1939, 59, 61—72, 73—78).—Theoretical considerations. A. T. P.

Pyrazole synthesis. IV. Action of α -halogenohydrazones on sodium derivatives of β -

ketonic esters. V. Action of α -halogenohydrazones on sodium salts of *sym*.- β -diketones. VI. Action of α -halogenohydrazones on sodium salts of *as*.- β -diketones. R. FUSCO (Gazzetta, 1939, 69, 344—352, 353—364, 364—378; cf. A., 1938, II, 206).—IV. In EtOH, $\text{COMe}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ or $\text{COPh}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ with $\text{CPhCl}\cdot\text{N}\cdot\text{NHPh}$ (I) gives Et 1 : 3-diphenyl-5-methyl- or 1 : 3 : 5-triphenyl-pyrazolone-4-carboxylate, respectively. With $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CBr}\cdot\text{CO}_2\text{Et}$ (II), the products are the *Et*₂ esters, m.p. 98—99° and 90°, respectively, of 1-p-nitrophenyl-5-methyl- (III), m.p. 265° (decomp.), and 5-phenyl-1-p-nitrophenyl-pyrazole-3 : 4-dicarboxylic acid (IV), m.p. 215° (decomp.). Above the m.p., (III) and (IV) lose CO_2 , giving the corresponding 4-carboxylic acids, m.p. 227—231° and 248°. $\text{KMnO}_4\text{--KOH}$ oxidation of (III) gives 1-p-nitrophenyltriazole-3 : 4 : 5-tricarboxylic acid, m.p. 70—72° (+ $3\text{H}_2\text{O}$), 204—205° (anhyd.), of which the *Et*₂ ester, m.p. 76°, is obtained from (I) and $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$.

V. (I) and CH_2Ac_2 with NaOEt in EtOH give 4-acetyl-1 : 3-diphenyl-5-methylpyrazole, m.p. 88° (phenylhydrazone, m.p. 182°), or, in EtOH- Et_2O , a product, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ (? 3 : 5-diphenyl-2-methyl-2-acetonyl-2 : 3-dihydro-1 : 3 : 4-oxadiazole), m.p. 156°, easily decomposed into $\text{NHPh}\cdot\text{NHBz}$ and (I). With CHNaBz_2 in EtOH, (I) gives 4-benzoyl-1 : 3 : 5-triphenylpyrazole, m.p. 174°. With NaOEt in EtOH, (II) and CH_2Ac_2 give the *Et* ester, m.p. 173—174° [*p*-nitrophenylhydrazone, m.p. 310° (decomp. from 300°)], of the -3-carboxylic acid (V), m.p. 205° (decomp.) (*p*-nitrophenylhydrazone, m.p. 260—262°), of 4-acetyl-1-p-nitrophenylpyrazole (VI), m.p. 156° (obtained by decarboxylation at 200—210°). In 80% HNO_3 , (V) and (VI) are oxidised to 1-p-nitrophenyl-5-methylpyrazole-3 : 4-dicarboxylic acid, m.p. 265° (decomp.), and 4-carboxylic acid, m.p. 230°, respectively. With CHNaBz_2 , (II) gives the *Et* ester, m.p. 174°, of the -3-carboxylic acid, m.p. 233° (decomp.), of 4-benzoyl-5-phenyl-1-p-nitrophenylpyrazole, m.p. 163—164° (obtained by decarboxylation); the last three compounds do not react with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$.

VI. With $\text{COPh}\cdot\text{CHNa}\cdot\text{CHO}$ in EtOH, EtOH- C_6H_6 , or EtOH- Et_2O , (II) gives the *Et* ester, m.p. 165° (*p*-nitrophenylhydrazone, m.p. 283°), of the 3-carboxylic acid (VII), m.p. 263° (decomp.) (NH_4 salt, decomp. 255—268°; *p*-nitrophenylhydrazone, m.p. 300°), of 4-benzoyl-1-p-nitrophenylpyrazole, m.p. 195—197° [*p*-nitrophenylhydrazone, m.p. 251° (sinters ~220°)]. With $\text{COPh}\cdot\text{CH}_2\cdot\text{COMe}$ and NaOEt in EtOH, (II) gives the *Et* ester, m.p. 170°, of the -3-carboxylic acid (VIII), m.p. 200° (decomp.) (no *p*-nitrophenylhydrazone obtained from ester or acid), of 4-benzoyl-1-p-nitrophenyl-5-methylpyrazole, m.p. 155—156°. With aq. $\text{KMnO}_4\text{--KOH}$, (VIII) yields (VII). With $\text{COPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ and NaOMe in MeOH, (II) gives 5-carbomethoxy-3-carbethoxy-4-benzoyl-1-p-nitrophenylpyrazole, m.p. 136—138°, hydrolysed to 4-benzoyl-1-p-nitrophenylpyrazole-3 : 5-dicarboxylic acid (+ H_2O lost at ~140°), m.p. 185—190° (decomp.) (no *p*-nitrophenylhydrazone obtained from ester or acid), decarboxylated to (VII). With $\text{COMe}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ [from COMe_2 , $\text{Et}_2\text{C}_2\text{O}_4$, and NaOMe in MeOH] in C_6H_6 , EtOH, or (slowly) in Et_2O , (II) gives 5-carbomethoxy-3-carbethoxy-4-acetyl-1-

p-nitrophenylpyrazole, m.p. 158—159° (no *p*-nitrophenylhydrazone), hydrolysed to 4-acetyl-1-p-nitrophenylpyrazole-3 : 5-dicarboxylic acid (+ H_2O , lost at 140°), m.p. 176° (decomp.) [*p*-nitrophenylhydrazone, m.p. 258—261° (softens 238°)], oxidised (HNO_3) to the 3 : 4 : 5-tricarboxylic acid. The following order of reactivity for the formation of pyrazole and isooxazole rings is proposed : $\text{CHO} > \text{CO}\cdot\text{CO}_2\text{R} > \text{Ac} > \text{Bz} > \text{CN} > \text{CO}_2\text{Et} > \text{CO}\cdot\text{NH}_2$. E. W. W.

Action of hydriodic acid on cycloglycylglycine [diketopiperazine] and biological significance of product obtained. V. S. ISUPOV (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 158—162).—Diketopiperazine with aq. 25% HI at 100° for 6 hr. yields a substance (I), $\text{C}_9\text{H}_{21}\text{O}_7\text{N}_5\text{I}_2$, m.p. 224°, which when boiled with EtOH gives a substance, $\text{C}_4\text{H}_{10}\text{O}_4\text{N}_2$. The formation and structure of these compounds are discussed. NH_2 -acids and polypeptides do not form I-compounds under the above conditions. (I) causes a decrease in blood pressure when injected intravenously into cats [(II) has no effect], and when introduced into the cavities of axolotls transforms them into amblystomes in 38 days. J. N. A.

Polarisation in heterocyclic rings with aromatic character. III. Polarisation of the pyrimidine ring. E. OCHIAI and M. YANAI (J. Pharm. Soc. Japan, 1939, 59, 97—104).— NaNH_2 and 6-methylpyrimidine in decahydronaphthalene at ~130° briskly evolve H_2 and give 2-amino-6-methylpyrimidine (I), m.p. 158—159°, 2 : 4-diamino-6-methylpyrimidine, m.p. 183—185° (hydrochloride, m.p. 253—255°), a dimethyldipyrimidyl, $\text{C}_{10}\text{H}_{10}\text{N}_4$, b.p. 110—120°/0.002 mm. (picrate, decomp. 212—214°; hydrobromide, decomp. 209—210°; mercurichloride, decomp. 250—251°), and a viscous liquid, b.p. 180—200°/0.002 mm., which does not afford cryst. salts. Hence $\text{C}_{(2)}$, $\text{C}_{(4)}$, and $\text{C}_{(6)}$ of pyrimidine show electrophilic activity and $\text{C}_{(2)}$ is highly active. 2 : 4 : 6-Trimethylpyrimidine and $\text{CH}_2\text{Ph}\cdot\text{COBr}$ in abs. EtOH yield 2 : 4 : 6-trimethylpyrimidine hydrobromide, 4' : 6'-dimethylpyrimidino-1' : 2'-1 : 5-3-phenylpyrrole, b.p. 180—200°/0.005 mm. (picrate, decomp. 220—223°), and (probably) phenylacetonylpyrrole, m.p. 178—180° (mono-*p*-nitrophenylhydrazone, m.p. 233—235°). $\text{CH}_2\text{Ph}\cdot\text{COBr}$ and (I) in hot EtOH give 4'-phenyliminazolo-1' : 2'-1 : 2-6-methylpyrimidine, m.p. 223—224° (hydrochloride, decomp. 240—243°; hydrobromide, decomp. 260—261°; picrate, decomp. 239—240.5°; mercurichloride, decomp. 259—260°). 4-Amino-6-methylpyrimidine and $\text{CH}_2\text{Ph}\cdot\text{COBr}$ give some hydrobromide, decomp. 226—227°, and the phenacylobromide, decomp. 263—264°, converted by warm aq. NaHCO_3 into 4'-phenyliminazolo-1' : 2'-3 : 4-6-methylpyrimidine, decomp. 244° (picrate, decomp. 212—214°; hydrochloride, decomp. 247—250°). The base is relatively unstable and passes when recrystallised into a black, tarry mass. It is unchanged by NaHCO_3 , KHCO_3 , $\text{KOH}\cdot\text{H}_2\text{O}$, or $\text{KOH}\cdot\text{EtOH}$. H. W.

Action of Grignard's reagent on the carbethoxy side-chain of halogenated [ethyl] pyrimidine[acetates]. E. OCHIAI and Z. ITIKAWA (J. Pharm. Soc. Japan, 1938, 58, 168—171).—*Et* 4-chloro-2-methylpyrimidine-5-acetate, m.p. 39—40° (from the 4-OH derivative and POCl_3), and MgMeI

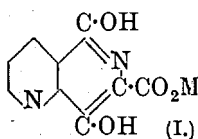
give 4-chloro-2-methyl-5- β -hydroxy- β -methylpropylpyrimidine (I), b.p. 160—240°/0.01 mm. (hydrochloride, decomp. 267—268°), and a little 4-chloro-5-acetonyl-2-methylpyrimidine, decomp. 254° (semicarbazone, decomp. 174—175°). 4-Amino-2-methyl-5- β -hydroxy- β -methylpropylpyrimidine, m.p. 160—162° [from (I) and EtOH-NH₃ at 100°], and AcOH-HBr at 100° afford 4-amino-2-methyl-5- β -bromo- β -methylpropylpyrimidine hydrobromide, decomp. 187—188°, which does not give a quaternary salt with 4-methyl-5- β -hydroxyethylthiazole but loses HBr to yield 4-amino-2-methyl-5- Δ^1 -isobutenylpyrimidine (picrate, decomp. 202°).

H. B.

Condensation of 2:4:6-trimethylpyrimidine and benzaldehyde. II. E. OCHIAI and M. YANAI (J. Pharm. Soc. Japan, 1938, 58, 76—79).—This condensation gives 4:6-dimethyl-2-styryl- (I), new m.p. 57—58°, 6-methyl-2:4-distyryl- (II), m.p. 177—178.5°, and 2:4:6-tristyryl-pyrimidine. With O₂-O₃ in CHCl₃, (II) gives PhCHO and 6-methylpyrimidine-2:4-dialdehyde (bis-p-nitrophenylhydrazone, decomp. 290—292°), oxidised by KMnO₄ to the -2:4-dicarboxylic acid (+2H₂O), decomp. 195—197°. With O₂-O₃ (I) similarly gives 4:6-dimethylpyrimidine-2-aldehyde (p-nitrophenylhydrazone, m.p. 215—216°), oxidised to the -2-carboxylic acid. The following data are also given: 2:4:6-trimethylpyrimidine, m.p. 199—200° (picrate, decomp. 222—224°); pyrimidine-2:4:6-trialdehyde (2-p-nitrophenylhydrazone, decomp. >320°), and -2:4:6-tricarboxylic acid, decomp. >320°; picrate, decomp. 187—189° (?), of (I).

E. W. W.

2:5-Naphthyridine derivatives. II. E. OCHIAI and H. MIYAKI (J. Pharm. Soc. Japan, 1938, 58, 207—211; cf. A., 1937, II, 467).—Hydrolysis of Me 1:4-dihydroxy-2:5-naphthyridine-3-carboxylate (I) (Ac derivative, m.p. 225°) by strong acids gives 1:4-dihydroxy-2:5-naphthyridine (II), m.p. >310° [picrate, m.p. 230° (decomp.)]; Ac derivative, m.p. 216—217° (decomp.). Both (I) and (II) are



phenolic, giving greenish-blue FeCl₃ colours, being indifferent to CO₂ reagents, and not allowing replacement of the lactim O by S. POCl₃ converts (II) into 1-chloro-4-hydroxy-2:5-naphthyridine (III), m.p. 215°, the Cl of which resists replacement by H. The 3-CO₂Me-derivative (IV) of (III) with NH₃-EtOH gives only 1-chloro-4-hydroxy-2:5-naphthyridine-3-carboxylamide, m.p. 288—289° (decomp.). The Ac derivative of (IV) resists replacement of Cl by SH. H₂-PtO₂ in AcOH reduces only the C₅H₅N ring, giving 1-chloro-4-hydroxy-5:6:7:8-tetrahydro-3:5-naphthyridine, m.p. 149°, and its 3-CO₂Me-derivative, m.p. 206°.

R. S. C.

Reaction between *m*-phenylenediamine and ethyl acetoacetate. G. JACINI (Gazzetta, 1939, 69, 405—408).—This reaction, in AcOH at 50°, gives Et₂-*m*-phenylenebisaminocrotonate, new m.p. 31° (cf. Backeberg, A., 1936, 64). At 200—250°, this gives 4:8-dihydroxy-2:6-dimethyl-1:5-phenanthroline, decomp. 330°, stable to CrO₃ in AcOH or H₂SO₄, which is oxidised by alkaline KMnO₄, with POCl₃ gives 4:8-dichloro-2:6-dimethyl-1:5-phenanthroline, m.p.

168°, and when distilled over Zn gives 2:6-dimethylphenanthroline.

E. W. W.

1-Aminoindolizine derivatives. E. OCHIAI, M. WADA, M. SUZUKI, and T. NISHIZAWA (J. Pharm. Soc. Japan, 1938, 58, 172—174).—Attempts to synthesise compounds containing the annexed ring system from derivatives of 1-aminoindolizine were unsuccessful. The Schiff base, m.p. 120°, from AcCO₂Me and 1-amino-3-acetyl-2-methylindolizine (I) (CHPh₂, m.p. 129—130°, and N-Ac, m.p. 219°, derivative) with H₂SO₄, AcOH, AlBr₃, ZnCl₂, or NaOEt undergoes no condensation. The N-chloroacetyl derivative, m.p. 223° (decomp.), of (I) is either unaffected or resinified by AlCl₃ in CS₂, PhNO₂, or C₂H₂Cl₄.

H. B.

Synthesis of 3:4:8:9-dibenzo-5:10-diazapyrene. G. R. CLEMO and E. C. DAWSON (J.C.S., 1939, 1114—1118).—1:5-Dianilinonaphthalene, m.p. 214°, prepared from the OH-compound and NH₂Ph, is oxidised (O₂-AlCl₃) to 3:4:8:9-dibenzo-5:10-diazapyrene, m.p. 362°. PbO₂ and β -C₁₀H₇NH₂ give 1:2:6:7-dibenzophenazine and a substance, C₂₀H₁₁N₂, m.p. 195° (? 5:10-dihydro-1:2:6:7-dibenzophenazine). N₂H₄ and β -C₁₀H₇OH, followed by HCl, yield 2:2'-diamino-1:1'-dinaphthyl (45% yield), which could not be cyclised.

F. R. S.

Sulphoxytriazine [5-keto-3-thion-2:3:4:5-tetrahydro-1:2:4-triazine] ethers. E. CATTELAINE (Compt. rend., 1939, 208, 1912—1914; cf. A., 1928, 308).—Alkylation of the appropriate *S*-monoethers of 6-benzylsulphoxytriazine (cf. A., 1939, II, 390) in a neutral medium leads to 3-benzylthiol-2:6-dibenzyl- (I), m.p. 106°, 3-methylthiol-6-benzyl-2-methyl-, m.p. 116.5°, and 3-ethylthiol-6-benzyl-2-ethylsulphoxytriazine, a liquid, all of which are hydrolysed (EtOH-HCl) to the 2-mono-ether and a mercaptan, thereby proving the structure of the di-ethers. 3-Benzylthiol-6-benzylsulphoxytriazine (II) has m.p. 167°. (I) and (II) when reduced give 3-benzylthiol-2:6-dibenzyl-, a liquid, and 3-benzylthiol-6-benzyl-, m.p. 125°, 1:6-dihydrosulphoxytriazine respectively, which do not behave as mono-acids and are oxidised by I-NaOH to (I) and (II), respectively.

J. L. D.

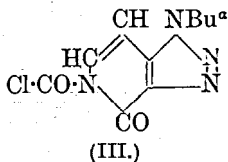
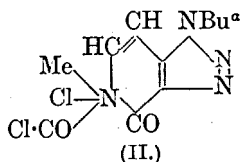
Condensation of formaldehyde with thioarylhydrazines. H. WUYTS and (MLLE.) A. L. LACOURT (Bull. Soc. chim. Belg., 1939, 48, 165—175; cf. A., 1934, 537; A., 1937, II, 434).—Equimols. of the appropriate thioaryl- α -phenylhydrazine and CH₂O in EtOH-HCl afford 1:5-di-(thioacetyl)-, m.p. 186°, -(thiophenylacetyl)- (II), m.p. 172°, -(thiobenzoyl)- (III), m.p. 187°, -(thio-*p*-toluoyl)- (IV), m.p. 190°, and -(thio- α -naphthoyl)-2:4-diphenylhexahydrotetrazine, m.p. 200°, of type R-CS-N<CH₂N(CSR)NPh-CH₂>NPh.

In contrast with the lower-melting thiodiazolines (*loc. cit.*) (made with less HCl), the above are almost insol. in Et₂O or EtOH, and are crystallised from C₅H₅N-H₂O. 3-Phenyl-5-benzyl- or -*p*-tolyl-2:3-dihydro-1:3:4-thiodiazole and HCO₂H (*d* 1.22) at 90° or 110° afford (II) or (IV), respectively. (III) and I-CHCl₃ give a I₁₀-derivative, m.p. 195°, transformed by dis-

solution in COMe_2 and pptn. with Et_2O into a I_6 -derivative, m.p. 225° (decomp.). A. T. P.

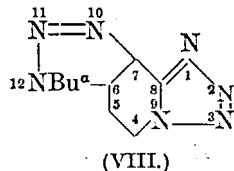
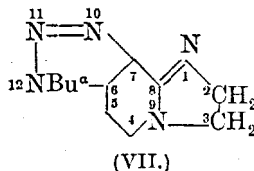
Attempted hydrogenation of 3-methylxanthine. T. B. JOHNSON and J. C. AMBELANG (Science, 1939, 90, 68—69).—Xanthine (I) and 3-methylxanthine (II) resist structural changes when hydrogenated in presence of certain catalysts. They are unaltered by exposure in AcOH to H_2 for 8 hr. in presence of Adams' Pt (1.5—2.0 atm.). Shaking with H_2 for 10 hr. at $200^\circ/160$ —200 atm. in abs. EtOH in presence of Raney Ni partly destroys (I) and (II), but 60% of (II) was recovered unchanged. Catalytic hydrogenation of (I) at different pressures and temp. in presence of Cu—Cr oxide catalyst resulted in extensive decomp. Glyoxaline, 2 : 4 : 5-trimethylglyoxaline, histidine, lysidine, and benziminazole are not reduced in presence of Pt-black. Benziminazole-benzimide could not be hydrogenated using Adams' Pt, Raney Ni, or Cu—Cr oxide. L. S. T.

Pyridino-3 : 4-triazole series. III. O. BREMER (Annalen, 1939, 539, 276—296; cf. A., 1937, II, 308).—Numerous derivatives of pyridino-3' : 4'-4 : 5-triazole are prepared; all structures, if not obvious, are proved by the ring-closures described. They differ from isoquinoline derivatives in many respects. Halogen in position 2 of the $\text{C}_5\text{H}_5\text{N}$ ring is very reactive, but in position 5 is extremely inert. Cl is introduced into 2'-keto-1'-methyl-1-n-butyl-1' : 2'-dihydropyridino-3' : 4'-4 : 5-triazole by PCl_5 at 100° , but COCl_2 in PhOH gives a substance, converted by H_2O or EtOH into 2'-hydroxy-1-n-butylpyridino-3' : 4'-4 : 5-triazole (I), m.p. 223° , probably by way of (II) and (III) and also obtained from the 2'-Cl-compound



by 15% $\text{KOH-MeOH-H}_2\text{O}$ at 100° . Br-KOAc in AcOH converts (I) into 5'-bromo-2'-hydroxy-1-n-butylpyridino-3' : 4'-4 : 5-triazole, m.p. 163° , and fuming HNO_3 in conc. H_2SO_4 at 5 — 10° gives the 5'- NO_2 -derivative, m.p. 198° . 3-Nitro-4-butylaminopyridine is reduced and chlorinated by SnCl_2 in hot fuming HCl , giving 2-chloro-3-amino-4-n-butylaminopyridine, m.p. 107 — 108° (hydrochloride, m.p. 223 — 224°), converted by diazotisation into 2'-chloro-1-n-butylpyridino-3' : 4'-4 : 5-triazole, m.p. 10° , b.p. 171 — $172^\circ/3$ mm. This is converted by NaOEt-EtOH at 100° into the 2'- OEt -, m.p. 50 — 51° , by 32% KSH-MeOH at 100° into the 2'- SH -, m.p. 203 — 204° , by 10% $\text{NH}_3\text{-EtOH}$ at 150 — 160° into the 2'- NH_2 - (IV), m.p. 176 — 177° , by 33% $\text{NH}_2\text{Me-EtOH}$ at 150 — 160° into the 2'- NHMe -, m.p. 93 — 94° , by 25% $\text{NHMe}_2\text{-EtOH}$ at 150 — 160° into the 2'- NMe_2 -, m.p. 119 — 120° , b.p. 160 — $161^\circ/3$ mm., by $\text{NH}_2\cdot[\text{CH}_2]_2\text{NEt}_2$ at 150 — 160° into the 2'- β -diethylaminoethylamino-, b.p. 209 — $210^\circ/3$ mm., by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH at room temp. into the 2'- $\text{NH}_2\cdot\text{NH}$ - (V), m.p. 80° , by cyclohexylamine and a little EtOH at 150 — 160° into the 2'-cyclohexylamino-, m.p. 74° , and by $\text{OH}\cdot[\text{CH}_2]_2\text{NH}_2$ and a little EtOH at

150 — 160° into the 2'- β -hydroxyethylamino-derivative, m.p. 78 — 79° {hydrochloride, m.p. 193 — 194° ; converted by SOCl_2 at 100° into the 2'- β -chloroethylamino-derivative (VI), cryst. [hydrochloride, m.p. 190° (decomp.)]}. Diazotisation of 2 : 5-dichloro-3-amino-4-butylaminopyridine (prep. from 5-chloro-3-nitro-4-butylaminopyridine by $\text{SnCl}_2\text{-HCl}$, b.p. 163 — $164^\circ/3$ mm., m.p. $<0^\circ$, gives 2' : 5'-dichloro-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 48° , b.p. $198^\circ/3$ mm., which with $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ at 130 — 140° gives 5'-chloro-2'-p-anisidino-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 103 — 104° . 2-Chloro-5-bromo-3-amino-4-n-butylaminopyridine (similarly prepared), m.p. 45° [hydrochloride, m.p. 167° (decomp.)], gives similarly 2'-chloro-5'-bromo-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 66 — 67° , and thence (by 10% $\text{NH}_3\text{-EtOH}$ at 120 — 130°) 2'-chloro-5'-amino-, m.p. 222° [also obtained from (IV) by Br-AcOH at 100° , and (by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH at room temp.) 2'-chloro-5'-hydrazino-1-n-butylpyridino-3' : 4'-4 : 5-triazole, m.p. 124° . With fuming HNO_3 in conc. H_2SO_4 , (IV) yields in a short time 2'-nitroamino-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 165 — 166° (decomp.), or after being kept overnight 5'-nitro-2'-amino-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 259° , reduced by SnCl_2 in fuming HCl at 100° to the 2' : 5'-(NH_2) $_2$ -derivative, m.p. 202 — 203° [Ac_2 derivative, m.p. 205 — 206° ; monohydrochloride, m.p. 266 — 267° (decomp.)], which consumes 1 HNO_2 and then with a further mol. of diamine gives the diazoamino-compound, cryst., also obtained directly by diazotisation in presence of insufficient HCl . 5-Bromo-1-n-butylpyridino-3' : 4'-4 : 5-triazine, m.p. 43 — 44° (picrate, m.p. 122 — 123°), is obtained from 4-chloro-5-bromo-3-nitropyridine by way of 5-bromo-3-nitro-, an oil, and 5-bromo-3-amino-4-n-butylaminopyridine, m.p. 46° , b.p. $163^\circ/3$ mm.; with $\text{NH}_3\text{-EtOH}$ at 170 — 180° it affords the 5- NH_2 -derivative, m.p. 148° , converted by HNO_2 into the 5- OH -derivative, m.p. 109 — 110° . When heated at 170 — 180° , (VI) gives impure 1'-n-butyltriazino-4'' : 5''-3' : 4'-pyridino-1' : 2'-1 : 2-4 : 5-dihydroglyoxaline (VII), cryst. (ethiodide, m.p. 176° ; author's numbering as shown). Diazotisation of (V) gives



1'-n-butyltriazino-4'' : 5''-3' : 4'-pyridino-1' : 2'-1 : 2-4 : 5-dihydroglyoxaline (VIII) (author's numbering as shown), m.p. 157 — 158° , and the 5'- Br -derivative, m.p. 114° , is similarly prepared. Diazotisation of 5-nitro-2-hydrazinopyridine gives 5'-nitropyridino-1' : 2'-1 : 2-4 : 5-dihydroglyoxaline, m.p. 142 — 143° (decomp.). The K salt of 5'-bromopyridino-3' : 4'-4 : 5-triazine with Bu^aI in MeOH at 150 — 160° gives the base, $\text{CH}=\text{CBr}\cdot\text{C}\cdot\text{N}\cdot\text{NBu}^a\cdot\text{CH}\cdot\text{C}\cdot\text{N}\cdot\text{N}$ ("5'-bromo-1-n-butylpyridino-3' : 4'-4 : 5-triazole"), m.p. 106° , b.p. 167 — $168^\circ/3$ mm. (picrate, m.p. 134 — 144°). In the formation of (IX) and the tricyclic compounds, the $\text{C}_5\text{H}_5\text{N}$ derivatives react in tautomeric forms. R. S. C.

Anomalous decomposition of the tetrazo-derivative of 2:2'-diamino-1:1'-dinaphthyl. VI. Dehydrogenating action of thionyl chloride on an ethylenic double linkage. A. CORBELLINI, C. GHITOLDI, and F. CHEVALLARD (Gazzetta, 1939, 69, 291—301).—The acid $C_{20}H_{12}O_2N_2$ obtained by oxidation of *cis-o*-(4:5:1':2'-naphthopyrazolyl)-cinnamic acid (I) by $SOCl_2$ (A., 1939, II, 391) is shown to be the corresponding -*propionic acid* (II). The Et ester (III) of (II) is oxidised by $KMnO_4$ in C_2H_5N to the corresponding -benzoic acid (IV) (A., 1936, 979), also obtained by similar oxidation of the Et ester of (I). With *iso*- $C_5H_{11}OH-N_2H_4.H_2O$, (III) gives 3-*o*-(4':5':1'':2'-naphthopyrazolyl-3')-phenylpyrazol-5-one, m.p. 295° [hydrochloride, m.p. 191°; *N*O-derivative, m.p. 186° (decomp.); PhN_2 -compound, m.p. 273.5°; Ac derivative, m.p. 85—92°]. The acid chloride of (I) with $N_2H_4.H_2O$ in $CHCl_3$ gives the hydrazide, m.p. 261—262° (decomp. from 250°), of (I). With KOH -*iso*- $C_5H_{11}OH$, (I) gives (IV), AcOH, and a substance, m.p. 228°. E. W. W.

Water-soluble c-hæmin from blood.—See A., 1939, III, 552.

Action of nitric acid on phenacylacetone. II. S. CUSMANO (Gazzetta, 1939, 69, 214—221).—Angeli's product, " $C_{22}H_{18}O_{11}N_4$," m.p. 210° (A., 1893, i, 197), from $COPh[CH_2]_2COMe$ and HNO_3 (*d* 1.45) is identified as 5-*p*-nitrophenylisooxazole-3-carboxylic acid (I) [Et ester (II), m.p. 183°; $NHPh.NH_2$ salt, m.p. 168—170° (decomp.)], oxidised by alkaline $KMnO_4$ to *p*- $NO_2.C_6H_4.CO_2H$. With HNO_3 (*d* 1.45), $COPh.CH_2.CH(COMe).CO_2Et$ gives (II), and 5-phenylisooxazole-3-carboxylic acid gives, at >60°, (II), or, at the b.p., (I). E. W. W.

New syntheses of isooxazolepolycarboxylic acids. I. L. PANIZZI (Gazzetta, 1939, 69, 322—329).— $CHPh.CH.CCl.N.OH$ and $COMe.CH.Na.CO_2Et$ (I) give Et 5-methyl-3-styrylisooxazole-4-carboxylate, m.p. 60—60.5°, easily hydrolysed (KOH -MeOH) to the 4-carboxylic acid, m.p. 240—241° (decomp.) (acid chloride, m.p. 98—99°; amide, m.p. 226.5—227.5°; anilide, m.p. 178—178.5°), which is oxidised ($KMnO_4$ in aq. Na_2CO_3) to 5-methylisooxazole-3:4-dicarboxylic acid [dichloride; diamide, m.p. 219—220°; dianilide, m.p. 177—178° (decomp.)], of which the Et₂ ester is prepared from $CO_2Et.CCl.N.OH$ and (I). E. W. W.

isoBenzoxazoles. II. W. BORSCHKE and W. SCRIBA (Annalen, 1939, 540, 83—98; cf. A., 1921, i, 652).—Formation of isobenzoxazoles from *o*-halogenophenyl ketoximes often depends on the alkali used. Addition of PCl_5 , followed by $AlCl_3$, to *o*- $C_6H_4Br.CO_2H$ in C_6H_6 gives ~80% of *o*- $C_6H_4Br.COPh$ (I), b.p. 190°/14 mm., the oxime, m.p. 132°, of which in hot KOH -MeOH (1:4) gives 2-phenylisobenzoxazole (II), m.p. 83°, obtained also from *o*- $C_6H_4F.CPh.N.OH$. *o*- $C_6H_4Br.COCl$ (0.1), Ph_2 (0.3), and $AlCl_3$ (0.2 mol.) at 100° give 4-*o*-bromobenzoyldiphenyl, m.p. 90°, b.p. 230—235°/1 mm., the oxime, m.p. 187—188°, of which with 2*N*-aq. KOH -MeOH (1:1) at 140° gives 4-2'-isobenzoxazolyldiphenyl, m.p. 119—120°, but the crude ketone with $NH_2OH.HCl$ and KOH in boiling MeOH gives also

some (?) 2-2'-isobenzoxazolyldiphenyl, m.p. 100—101°. An excess of *o*- $C_6H_4Br.COCl$ yields 4:4'-*di-o*-bromobenzoyldiphenyl, m.p. 155—156°, the dioxime, m.p. 229—230°, and thence 4:4'-*di*-2-isobenzoxazolyldiphenyl, m.p. 235—236°. With Br -AcOH at room temp., (II) gives the 4-*Br*-, m.p. 88—89°, and with $KNO_3-H_2SO_4$ gives the mixed $(NO_2)_2$ -derivatives (mainly m.p. 164—165°; a part has m.p. up to 190°; cf. lit.). Na -EtOH reduces (II) to 2-hydroxybenzhydramine, m.p. 104—105° (*Ac*₂, m.p. 141—141.5°, and *ON*-Bz₂ derivative, new m.p. 175°, hydrolysed by KOH -MeOH to the *N*-Bz derivative, new m.p. 213—214°; $CH_2N_2-COME_2$ gives *o*-methoxybenzhydramine, m.p. 93—94°). $N_2H_4.H_2O$ at 200° converts (II) into $PhOH$, *o*-hydroxybenzophenoneazine, m.p. 273°, *o*-hydroxydiphenylmethane, b.p. 159—162°/12 mm., and a substance, m.p. 199—200°. $N_2H_4.H_2O$ and (I) at 200° give 3-phenylindazole (III), m.p. 115—116°, b.p. 220—225°/14 mm., and *o*-bromodiphenylmethane, m.p. 30—31°, b.p. 159—160°/14 mm. [$(NO_2)_2$ -derivative, m.p. 127—128°]. 5:2:1- $NO_2.C_6H_3Br.COPh$ (IV) and $N_2H_4.H_2O$ in MeOH at 140° give 5-nitro-3-phenylindazole, m.p. 187—188°, hydrogenated to the 5-*NH_2*-compound (*Bz* derivative, m.p. 252—253°), which with *iso*- $C_5H_{11}O.NO.HCl$ -MeOH and later HPO_2 yields (III): 3:5:2:1- $(NO_2)_2C_6H_2(OMe).COPh$ (V) and $N_2H_4.H_2O$ in boiling MeOH afford 5:7-dinitro-3-phenylindazole, m.p. 278—279°. $NHPh.NH_2.HCl$ and (IV) in MeOH at 140—150° give 5-nitro-1:3-diphenylisindazole, reduced by H_2 -Pd-C in EtOAc to the 5- NH_2 -compound (*Bz* derivative, m.p. 200—202°), which by a diazo-reaction gives 1:3-diphenylisindazole, m.p. 100—101°. With $NHPh.NH_2$ in boiling MeOH, (V) gives 5:7-dinitro-1:3-diphenylisindazole, m.p. 221—222°, and with $NH_2OH.HCl$ and $NaOMe$ in boiling MeOH gives 4:6-dinitro-2-phenylisobenzoxazole, m.p. 243° (decomp.). R. S. C.

Organic compounds of sulphur. XXVI. New method for the preparation of tetra-arylethylene sulphides. A. SCHÖNBERG and M. Z. BARAKAT (J.C.S., 1939, 1074—1075).—Tetra-arylethylene sulphides can be prepared from H_2S and boiling EtOH solutions of 2:2:5:5-tetra-aryl-2:5-dihydro-1:3:4-oxadiazoles. Tetra-phenyl-, *p*-tolyl-, m.p. 194—195°, and -anisyl-ethylene sulphide are prepared respectively from 2:2:5:5-tetra-phenyl-, *p*-tolyl-, m.p. 177—178° (efferv.), and -anisyl-2:5-dihydro-1:3:4-oxadiazole, m.p. 174° (decomp.). F. R. S.

3-Acylisooxazole. III. T. AJELLO and S. CUSMANO (Gazzetta, 1939, 69, 391—398).—3-Acetyl-5-methylisooxazole (or its oxime) with free NH_2OH in EtOH gives the oxime (I), m.p. 88° (*Bz* derivative, m.p. 112°) of 3-methyl-4-acetonyl-1:2:5-oxadiazole (II) (semicarbazone, m.p. 190°), to which (I) is hydrolysed by boiling dil. HCl . With $NaNO_2$ in AcOH, (II) gives its oximino-derivative, m.p. 153° (*Bz* derivative, m.p. 84°), which with free NH_2OH in EtOH forms 4-pyruvyl-3-methyl-1:2:5-oxadiazole dioxime, m.p. 172° (*Bz* derivative, m.p. 163°; *Ni* salt). Pyruvylacetone trioxime and boiling aq. KOH give (I). E. W. W.

Polarisation in heterocyclic rings of aromatic nature. II. Thiazole ring. E. OCHIAI and F.

NAGASAWA (J. Pharm. Soc. Japan, 1939, **59**, 43—49).—4-Methylthiazole (I) is not nitrated by $\text{HNO}_3\text{--H}_2\text{SO}_4$ at 0—100° (decomp. at 200°). With 20% oleum at 200° (no reaction at 100°) (I) gives 4-methylthiazole-5-sulphonic acid, m.p. 287—288° (Ba salt). 2-Thiol-4-methylthiazole and $\text{H}_2\text{O}_2\text{--KOH}$ give 4-methylthiazole-2-sulphonic acid, m.p. 207—211° (K salt, m.p. 273—277°). 2-Hydroxy-4-methylthiazole (II) and 20% oleum at 100° (bath) give 2-hydroxy-4-methylthiazole-5-sulphonic acid, m.p. 129—130° (+ H_2O), then solidifies and decomposes at ~212° (anhyd. form, decomp. ~225°) (Zn salt). (II) and $\text{HNO}_3\text{--H}_2\text{SO}_4$ at 0° give 5-nitro-2-hydroxy-4-methylthiazole, m.p. 158—159°. (I) and NaNH_2 in decahydronaphthalene at 150° afford 2-amino-4-methylthiazole (III), converted by 20% oleum at 0° or 100° (bath) respectively, into 4-methylthiazole-2-sulphonamic acid (IV), decomp. 256° (Ba salt), or 2-amino-4-methylthiazole-5-sulphonic acid (V), decomp. >340° (Ba salt), respectively; (IV) and H_2SO_4 at 100° (bath) give (V). (III) and $\text{HNO}_3\text{--H}_2\text{SO}_4$ give 5-nitro-2-nitroamino-4-methylthiazole, decomp. 185°. Theoretical aspects of the results are discussed.

A. T. P.

Benzthiazole derivatives. III. 1-Aminobenzthiazole derivatives. N. S. DROZDOV and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1939, **9**, 409—414).—1-Chloro-5-nitrobenzthiazole (I) is reduced (Fe in AcOH) to 1-chloro-5-aminobenzthiazole, m.p. 164°, from which 1-chloro-5-iodo- (II) or 1:5-dichlorobenzthiazole is prepared (Sandmeyer). When heated with a no. of NH_2Ph derivatives, (I) yields 5-nitro-1-anilino-, 1-o-toluidino-, m.p. 204—205°, and 1-p-dimethylaminoanilino-benzthiazole, m.p. 234°, whilst with arsanilic acid the product is 4-di-(5'-nitro-1'-benzthiazolyl)aminophenylarsinic acid, m.p. 63°. 1-Chlorobenzthiazole and γ -amino- α -piperidino- β -hydroxypropane heated at 100° for 1 hr. yield 1-(γ -piperidino- β -hydroxypropyl)aminobenzthiazole, an oil, whilst with β -amino- ϵ -diethylaminopentane (IV) the product is 1-(δ -diethylamino- α -methylbutyl)aminobenzthiazole, an oil. (I), (II), or (III) and (IV) similarly afford 5-nitro-, 5-iodo-, or 5-chloro-1-(δ -diethylamino- α -methylpropyl)aminobenzthiazole (oils). None of the products described possessed any antimalarial activity.

R. T.

Substitution of thiazole. E. OCHIAI and F. NAGASAWA (Ber., 1939, **72**, [B], 1470—1476).—The $\text{C}_{(2)}$ position of thiazole is active towards electron-donating reagents and the activity of the $\text{C}_{(2)}$ and $\text{C}_{(5)}$ positions towards electron acceptors is slight. The activity of the $\text{C}_{(5)}$ position towards electron acceptors is greatly enhanced by the presence of NH_2 or OH at $\text{C}_{(2)}$. 4-Methylthiazole is not attacked by Br in 20% H_2SO_4 or in CHCl_3 . Under similar conditions 5-bromo-2-amino-4-methylthiazole, decomp. 105—108.5°, is obtained from 2-amino-4-methylthiazole (II). 2-Hydroxy-4-methylthiazole (II) is converted by Br in CHCl_3 into 5-bromo-2-hydroxy-4-methylthiazole, decomp. 147.5°, and by the successive actions of $\text{Hg}(\text{OAc})_2$ in dil. AcOH, NaCl, and Br in CHCl_3 into dibromo-4-methylthiazole, decomp. 151°. AcCl , AlCl_3 , and (III) in PhNO_2 or $\text{C}_2\text{H}_2\text{Cl}_4$ afford 2-hydroxy-5-acetyl-4-methylthiazole (semicarbazone, decomp. 244°). Under similar conditions (II) yields 2-acetamido-4-

methylthiazole (IV), m.p. 134°, whereas (I), (IV), and 2-thiol-4-methylthiazole are largely unchanged. (III) is transformed by HCN and HCl in $\text{C}_2\text{H}_2\text{Cl}_4$, followed by H_2O , into 2-hydroxy-4-methylthiazole-5-aldehyde, decomp. 248° (p-nitrophenylhydrazones, decomp. 297—300°), also obtained by the action of KOH and CHCl_3 . In these circumstances (I) is unattacked.

H. W.

Syntheses of 2-thio-4-arylthiazolines. F. B. DAINS and O. A. KROBER (J. Amer. Chem. Soc., 1939, **61**, 1830—1831).— $\text{ArCO}\cdot\text{CH}_2\cdot\text{SCN}$ (prep. from $\text{ArCO}\cdot\text{CH}_2\text{Cl}$ by KCNS in hot EtOH) adds PhCS_2H to give $\text{NHBz}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\text{Ar}$, which with hot, dil. HCl yields BzOH and the 2-thio-4-arylthiazoline. MeCS_2H is also added, but the thiazoline is formed directly. The following are thus obtained: p-bromo-, m.p. 147°, p-chloro-, m.p. 135°, p-iodo-, m.p. 152°, p-methoxy-, m.p. 121°, and 4-nitro-, m.p. 119°, -phenacyl thiocyanate; phenacyl N-benzoyldithiocarbamate, m.p. 95°; p-chloro-, m.p. 148°, p-bromo-, m.p. 158°, and m-nitro-, m.p. 157°, -benzoyldithiocarbamate; 2-thio-4-p-chloro-, m.p. 148°, -4-p-bromo-, m.p. 214°, -4-p-iodo-, m.p. 220°, and -4-m-nitro-, m.p. 209°, -phenylthiazoline; 2-thio-4-phenyl-, m.p. 168°, and 2-thio-4-p-anisyl-thiazoline, m.p. 194°. $\text{COPh}\cdot\text{CHPh}\cdot\text{CNS}$ and MeCS_2H give 2-thio-4:5-diphenylthiazoline, m.p. 214° (2- CH_2Ph thioether, m.p. 106°), also obtained by PhCS_2H by way of an intermediate compound, m.p. 132—133° (cf. a compound, m.p. 137°, of Wheeler *et al.*, A., 1901, i, 705). $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{CNS}$ and PhCS_2H in C_6H_6 give rhodanine.

R. S. C.

Thiophen series. XLVIII. Thiophen analogues of 2:4:6-triphenylpyridine. W. STEINKOPF and W. POPP (Annalen, 1939, **540**, 24—30).—Thiophen-2-aldehyde (I), COPhMe , and 40% NaOH in boiling EtOH give α -diketo- α -diphenyl- γ -2-thienyl-n-pentane (II), m.p. 104°, and some α -diketo- δ -benzoyl- α -diphenyl- γ -di-2-thienyl-n-heptane, m.p. 251°. PhCHO and 2-acetylthiophen (III) give similarly α -diketo- α -di-2-thienyl- γ -phenyl-n-pentane (IV), m.p. 103°, and α -diketo- δ -2-thienoyl- γ -diphenyl- α -di-2-thienyl-n-heptane, m.p. 266°. (I) and (III) give α -diketo- α -tri-2-thienyl-n-pentane (V), m.p. 103°, and α -diketo- δ -2-thienoyl- α - γ - η -tetra-2-thienyl-n-heptane, m.p. 268°; furfuraldehyde and (III) give α -diketo- γ -2-furyl- α -di-2-thienyl-n-pentane (VI), m.p. 107°, and α -diketo- δ -2-thienoyl- γ -di-2-furyl- α -di-2-thienyl-n-heptane, m.p. 239°. NH_2OH , HCl and P_2O_5 in boiling abs. EtOH convert (II), (IV), and (V) into 2:6-diphenyl-4:2'-thienylpyridine, m.p. 157° (stable picrate, m.p. 212°; 3':5'- Br_2 -derivative, m.p. 163°), 4-phenyl-2:6-di-2'-thienylpyridine, m.p. 126° (unstable picrate, m.p. 166°; 3':5':3'':5''- Br_4 -derivative, m.p. 252°), and 2:4:6-tri-2'-thienylpyridine, m.p. 132° (unstable picrate, m.p. 148°; 3':5':3'':5''':5''':5''''- Br_6 -derivative, m.p. 316°); however, (VI) is resinified by this treatment. The picrates illustrate the decrease in basicity caused by $\text{C}_4\text{H}_3\text{S}$. The similar m.p. of the analogous ketones are lowered by admixture.

R. S. C.

Reaction of organic sulphur compounds with hydrogen peroxide. XIV. Constitution of anti-pyrene and related compounds. III. Mechan-

ism of desulphurisation of thiopyrine to antipyrine. XV. Compounds containing C:C·S. XVI. Synthesis of compounds of a new type. Thioperimino-acids. R. KITAMURA (J. Pharm. Soc. Japan, 1938, 58, 238—242, 243—246, 246—250). —XIV. Thiopyrine is converted into antipyrine by H_2O_2 more completely in presence of KOH than of K_2CO_3 in H_2O or 67% EtOH. The reaction is partly this conversion and partly formation of the trioxide, which yields antipyrine much more slowly.

XV. $\text{CHPh:C(SH)·CO}_2\text{H}$, $\text{SH·CPh:CH·CO}_2\text{H}$, and $\text{CHPh:CH·CH:C(SH)·CO}_2\text{H}$ are indifferent to alkaline H_2O_2 , which renders their structure doubtful. 10 cyclic compounds containing C:C·S react, although incompletely.

XVI. RCS·NH_2 and H_2O_2 (1 mol.) give thioperimino-acids, NH:CR·S·OH . Thus are prepared benzoic (I), m.p. 128—129°, phenylacetic (II), m.p. 135—136°, benzamidoacetic, m.p. 137—138°, and anilinophenylacetic, m.p. 124—125°, perimino-acid, all unstable in air or light. When heated, (I) gives PhCN and 3:5-diphenyl-1:2:4-thiadiazole (III) with a little SO_2 and NH_2Bz . (I) is sol. in 0.1N-KOH, but fairly rapidly decomposes therein. It is a weak acid, neutralising $\ll 1$ KOH (phenolphthalein). With Me_2SO_4 -KOH, (I) gives PhCN. The perimino-acids give an indigo FeCl_3 reaction, give platinichlorides and picrates, reduce AuCl_3 and AgNO_3 , and liberate a little I from acidified KI. They react with 3 H_2O_2 , giving H_2SO_4 quantitatively. With NH_2OH , (I) gives S and NH:CPh:NH·OH nearly quantitatively; with fuming HNO_3 and H_2SO_4 it gives S and $m\text{-NO}_2\text{·C}_6\text{H}_4\text{·CN}$; with boiling H_2O it gives PhCN, much (III), and a little NH_2Bz . Tautomeric forms, NH:CPh:S(H)·O , $^+\text{NH}_2\text{·CPh·SO}^-$, and $\text{NH}_2\text{·CPh:S·O}$, are probably present. With PhCN, NH_2Bz , or, best, PhCS·NH_2 at 115—120°, (I) gives (III). At 115—120° PhCS·NH_2 and (II) give 3-phenyl-5-benzyl-1:2:4-thiadiazole, m.p. 76—76.5°. (I) is an intermediate in the prep. of (III) from PhCS·NH_2 by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or I.

R. S. C.

Isosteric and structurally similar compounds. XII. Preparation and properties of 4:4'-dithiazolyl. H. ERLMEYER and H. UEBERWASSER (Helv. Chim. Acta, 1939, 22, 938—939).— HCS·NH_2 and $(\text{CO·CH}_2\text{Br})_2$ in Et_2O -EtOH and then in EtOH at 70° yield 4:4'-dithiazolyl (I), m.p. 170—171°. It is almost insol. in H_2O ; a colour is not developed in presence of FeSO_4 but (I) dissolves to a clear solution in the hot liquid and does not separate when the solution is cooled, thus indicating the possible formation of a colourless complex. There is no indication of the production of mixed crystals in the systems, (I)-2:2'-dithiazolyl or -2:2'-dipyridyl. H. W.

Synthetic experiments concerning eserine. VI. Constitution of methyleserethole. II. T. KOBAYASHI (Annalen, 1939, 539, 213—218).—The structure of methyleserethole (I) (A., 1938, II, 511) is confirmed by synthesis. 1:2-Dimethylindole with MgEtI in Et_2O , followed by $(\text{CH}_2\text{Br})_2$, gives 2:3-dimethyl-2- β -bromoethylindolenine, an oil, converted by NH_3 -EtOH at 100—105° into dinordeoxy-9-methyleseroline. Skatole similarly gives dinordeoxy-eseroline. $p\text{-OEt·C}_6\text{H}_4\text{·N}_2\text{Cl}$ and $\text{CH}_2\text{Ac·CO}_2\text{Et}$ in

aq. NaHCO_3 yield Et 5-ethoxyskatole-2-carboxylate, m.p. 171—172°, hydrolysed by alkali to the derived acid, m.p. 184—185° (decomp.) (Me ester, m.p. 178—179°), which at 200° gives 5-ethoxyskatole, m.p. 65—66°. With MgEtI in Et_2O , followed by $(\text{CH}_2\text{Br})_2$, this gives dinoreserethole or, if the indolenine is heated with NH_2Me or NHMe_2 in EtOH at 100—105°, isonoreserethole or (I), respectively. R. S. C.

Alkaloids of *Arthropytum leptocladum*, M. Pop. N. K. JURASCHEVSKI (J. Gen. Chem. Russ., 1939, 9, 595—597).—The dry leaves contained 0.7% of alkaloids, of which leptocladine, $\text{C}_{13}\text{H}_{16}\text{N}_2$, m.p. 109—110° [hydrochloride, m.p. 234—235° (decomp.)]; platinochloride, decomp. at 197—198°; picrate, sinters at 94—95°, m.p. 112—114°; Bz derivative, m.p. 132—133°, was isolated. R. T.

Lupine. XIII. Octalupine, an alkaloid from *Lupinus sericeus*, var. *flexuosus*, C. P. Smith. J. F. COUCH (J. Amer. Chem. Soc., 1939, 61, 1523—1524; cf. A., 1937, II, 434).—This plant yields octalupine, $\text{C}_{15}\text{H}_{22}\text{O}_2\text{N}_2$, m.p. 167.5—169.5°, b.p. 270—280°/6 mm., hygroscopic, $[\alpha]_D^{25} + 52.3^\circ$ in EtOH [dihydrochloride, $+1.5\text{H}_2\text{O}$ (0.5 H_2O lost at 110°), m.p. 298—299°, $[\alpha]_D^{25} + 36.3^\circ$ in H_2O , and $+ \text{H}_2\text{O}$, m.p. 288—289°; methiodide, m.p. 259°; aurichloride, m.p. 208—209°], which is stable to acid KMnO_4 , is reduced electrolytically to *d*-lupanine and sparteine, and is thus probably 2:16-diketosparteine. M.p. are corr. R. S. C.

Lupin alkaloids. XVIII. Synthesis of *allo*-lupinine. K. WINTERFELD and F. W. HOLSCHNEIDER (Arch. Pharm., 1939, 277, 221—237; cf. A., 1939, II, 395).— δ -Ethoxy- γ -valerolactone [prep. from $\text{CH}_2(\text{CO}_2\text{Et})_2$ and epichlorohydrin described] with Et picolinate and Na in C_6H_6 yields 2-pyridyl α -(δ -ethoxy- γ -valerolactonyl) ketone, b.p. 173—175°/0.4 mm. [HgCl_2 compound, m.p. 98—99°, clearing at 117°; *p*-sulphophenylhydrazone, m.p. 234—236° (decomp.); reineckate, m.p. 128—130°, decomp. 161—162°], which gives a red colour with FeCl_3 . With conc. HCl this yields 2-pyridyl γ -hydroxy- δ -ethoxy-*n*-butyl ketone, b.p. 110—120°/0.3 mm. [HgCl_2 compound, m.p. 75°, clearing at 103°; *p*-sulphophenylhydrazone, m.p. 235°, decomp. 248—252°; reineckate, m.p. 117°, decomp. 175—178°; 2:4-dinitrophenylhydrazone, m.p. 164—165°; phenylhydrazone and aurichloride (oils)], reduced (H_2 , PtO_2 in AcOH) to $\alpha\delta$ -dihydroxy- ϵ -ethoxy- α -2-piperidyl-*n*-propane [HgCl_2 compound, m.p. 129°; reineckate, m.p. 129—130°; Bz and PhCNO derivatives (oils)], which gives a deep red colour with Na nitroprusside and MeCHO. Cyclisation (PBr_3 followed by NaOEt) of this yields a mixture of 1-bromo-4-ethoxymethyl-octahydro- and 4-ethoxymethyl- Δ^{10} -hexahydro-quinolizine which with H_2 -Pd- CaCO_3 in EtOH-KOH yields 4-ethoxymethyl-, b.p. 142—144° (aurichloride, m.p. 85—87°; HgCl_2 compound, m.p. 125—126°; reineckate, m.p. 143—145°), hydrolysed (HI) to 4-hydroxymethyl-octahydroquinolizine (allolupinine), m.p. 123—125° [HgCl_2 compound, m.p. 201° (decomp.)]; reineckate, m.p. 152—153°; aurichloride and picrate (oils)]. A. Li.

Microcrystalline narcotine oxalate and phthalate. Y. VOLMAR, P. DUQUÉNOIS, and M. ELLERT (Compt. rend., 1939, 208, 2000—2001).—Equimol. amounts of *l*-narcotine (I) and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystallise from COMe_2 as *narcotine oxalate*, m.p. 174° , $[\alpha]_D^{25} +39.5^\circ$ in H_2O . Equimol. amounts of (I) and $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ crystallise from EtOH as *narcotine phthalate*, m.p. 160° , $[\alpha]_D^{25} +115^\circ$ in CHCl_3 . J. L. D.

Synthesis of hydrohydrastinine derivatives. M. TOMITA and M. SATOMI (J. Pharm. Soc. Japan, 1938, 58, 165—168).—Phenylacetomopiperonylamide, m.p. $97\text{--}98^\circ$ (from $\text{COPh} \cdot \text{CHN}_2$, homopiperonylamine, and Ag_2O), is converted (POCl_3 in PhMe) into 6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline (I) [*methiodide*, m.p. 258° (decomp.)], the methochloride of which is reduced (H_2 —PtO₂ or Sn—HCl) to 6:7-methylenedioxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (1-benzylhydrohydrastinine) [hydrochloride (+2H₂O), m.p. $110\text{--}120^\circ$; platinichloride, decomp. 205° ; *methiodide*, (+H₂O), m.p. 240° (decomp.)]. Reduction (H_2 , PtO₂) of (I) gives the 1:2:3:4-H₄-derivative (1-benzylnorhydrohydrastinine) [hydrochloride (+H₂O), m.p. $105\text{--}110^\circ$]. Similarly, *p*-anisylacetomopiperonylamide, m.p. 90° , is converted into 6:7-methylenedioxy-1-*p*-methoxybenzyl-3:4-dihydro- and -1:2:3:4-tetrahydro-isoquinoline [hydrochloride (+H₂O), m.p. 105°] and 6:7-methylenedioxy-1-*p*-methoxybenzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (1-*p*-methoxybenzylhydrohydrastinine) [platinichloride, decomp. 184° ; *methiodide*, m.p. 184° (decomp.)]. H. B.

Conversion of quinine into quinotoxin. A. MACHADO (Rev. Soc. Brasil. Quím., 1939, 8, 59—61).—Quinine in olive, cotton seed, or manobi oil at 140° for 1 hr. yields quinotoxin. F. R. G.

Syntheses in the series of Cinchona alkaloids. V. PRELOG, R. SEIWERTH, V. HAHN, and E. CERKOVNIKOV (Ber., 1939, 72, [B], 1325—1333).—Condensation of Et β -4-tetrahydropyranylethyl ketone with Et cinchoninate by NaOEt in C_6H_6 at $80\text{--}90^\circ$ gives 4'-quinolyl β -4-tetrahydropyranylethyl ketone (I), b.p. $187^\circ/0.02$ mm., m.p. 46° (hydrochloride, m.p. $166\text{--}166.5^\circ$; *picrate*, m.p. $154.5\text{--}155^\circ$; semicarbazone, m.p. 182° ; oximino-derivative, m.p. $158.5\text{--}159.5^\circ$). Under similar conditions Et quinate affords 6'-methoxy-4'-quinolyl β -4-tetrahydropyranylethyl ketone (II), b.p. $195\text{--}205^\circ/0.2$ mm., m.p. $54.5\text{--}55.5^\circ$ [hydrochloride, m.p. (indef.) $204\text{--}205^\circ$; *picrate*, m.p. $173\text{--}173.5^\circ$; oximino-derivative, m.p. $167.5\text{--}168^\circ$]. Reduction (PtO₂ in MeOH) of (I) yields α -4'-quinolyl- γ -4-tetrahydropyranylethylpropanol (III), m.p. $126.5\text{--}127^\circ$ (hydrochloride, m.p. $177\text{--}178^\circ$; *picrate*, m.p. $180\text{--}181^\circ$). Analogously (II) affords α -6'-methoxy-4'-quinolyl- γ -4-tetrahydropyranylethylpropanol (IV), non-cryst. (hydrochloride, m.p. $185\text{--}186^\circ$; *picrate*, m.p. $178\text{--}178.5^\circ$). The appropriate oximino-derivative is reduced (PtO₂ in EtOH) to β -amino- α -4'-quinolyl- (V), m.p. $171.5\text{--}172^\circ$ (corr.), and α -6'-methoxy-4'-quinolyl- (VI), m.p. (indef.). $180\text{--}181^\circ$, γ -4-tetrahydropyranylethylpropanol dihydrochloride. α -4-Tetrahydropyranylethyl- γ -4-quinolylpropane, b.p. $160\text{--}170^\circ/0.02$ mm. (*picrate*, m.p. 198.5°), obtained from the appropriate semicarbazone and NaOEt—EtOH at 180° , is transformed by 73%

HBr at 180° into α -bromo- δ -4'-quinolyl- γ - β' -bromoethylhexane hydrobromide, m.p. 114° , which is transformed by MeOH—NH₃ into α -4-piperidyl- γ -4'-quinolylpropane [rubatozan], b.p. $185^\circ/0.02$ mm. (dihydrochloride, m.p. 197° ; platinichloride, m.p. $>360^\circ$; *picrate*, m.p. $203\text{--}205^\circ$), and by K₂S in boiling EtOH into α -4-tetrahydropyranylethyl- γ -4'-quinolylpropane, m.p. 61° . 67% HBr at 100° converts (I) into α -bromo- ζ -4'-quinolyl- γ - β' -bromoethylheptan- ζ -one hydrobromide, m.p. $142\text{--}143^\circ$, which with Br—HBr at 100° gives α -dibromo- ζ -4'-quinolyl- γ - β' -bromoethylheptan- ζ -one hydrobromide, m.p. $136\text{--}137^\circ$, and with KOH—EtOH yields ζ -4-quinolyl- γ -vinyl- Δ^a -hexen- ζ -one, m.p. 59° (hydrobromide, m.p. 207° ; *picrate*, m.p. $204\text{--}208^\circ$). Et 2-ethoxycinchoninate is converted by condensation followed by hydrolysis with 10% HCl into 2'-hydroxy-4'-quinolyl β -4-tetrahydropyranylethyl ketone (VII), m.p. $179\text{--}180^\circ$ (H₂-derivative, m.p. $203\text{--}204^\circ$; oximino-derivative, m.p. 213°). (I), (II), (III), (IV), (V), and (VI) have no antimalarial action. H. W.

Cinchona alkaloids in pneumonia. VII. Amyl and hydroxyalkyl apocupreine ethers. M. H. GREEN, A. G. RENFREW, and C. L. BUTLER (J. Amer. Chem. Soc., 1939, 61, 1783—1784; cf. A., 1938, II, 341).—The following are prepared by standard methods: β -, b.p. $128\text{--}132^\circ/6$ mm., and δ -benzyloxy-n-butan- α -ol, b.p. $146\text{--}149^\circ/6$ mm.; γ -benzyloxy-n-butan- β -ol, b.p. $122\text{--}125^\circ/6$ mm.; CHET₂, m.p. 37° , β -hydroxy-n-propyl, m.p. 46° , and β -benzyloxy-sec-butyl, m.p. 47° , *p*-toluenesulphonate; apocupreine δ -benzyloxy-n-butyl, m.p. 104° , $[\alpha] -152^\circ$ in EtOH, β -hydroxy-n-propyl, m.p. 170° , $[\alpha] -180^\circ$ in EtOH (dihydrochloride, $[\alpha] -216^\circ$ in H₂O), β -hydroxyisobutyl, m.p. 102° , $[\alpha] -169^\circ$ in EtOH (dihydrochloride, $[\alpha] -218^\circ$ in H₂O), δ -hydroxy-n-butyl, m.p. 178° , $[\alpha] -179^\circ$ in EtOH (dihydrochloride, $[\alpha] -213^\circ$ in H₂O), α -hydroxymethyl-n-propyl, amorphous, $[\alpha] -165^\circ$ (dihydrochloride, $[\alpha] -202^\circ$ in H₂O), β -hydroxy-sec-butyl, amorphous, $[\alpha] -163^\circ$ (dihydrochloride, $[\alpha] -212^\circ$ in H₂O), *n*-amyl, m.p. 146° , $[\alpha] -178^\circ$ in EtOH (dihydrochloride, +1.5H₂O, $[\alpha] -230^\circ$ in H₂O), isoamyl, m.p. 175° , $[\alpha] -181^\circ$ in EtOH (dihydrochloride, +2H₂O, $[\alpha] -206^\circ$ in H₂O), β -methyl-n-butyl, m.p. 169° , $[\alpha] -172^\circ$ in EtOH (dihydrochloride, +H₂O, $[\alpha] -225^\circ$ in H₂O), sec-amyl, amorphous, $[\alpha] -163^\circ$ in EtOH (dihydrochloride, +2H₂O, $[\alpha] -212^\circ$ in H₂O), and α -ethyl-n-propyl, amorphous, $[\alpha] -150^\circ$ in EtOH (dihydrochloride, +1.5H₂O, $[\alpha] -213^\circ$ in H₂O), ether. The *in vitro* bacteriostatic activity and toxicity of the apocupreine alkyl and hydroxyalkyl ethers are recorded. OH reduces both effects. R. S. C.

Methiodides of quinidine and hydroquinidine. F. VON KONEK (Math. nat. Anz. ung. Akad. Wiss., 1936, 54, 821—829; Chem. Zentr., 1937, i, 1694).—Quinidine (I) [*methiodide*, m.p. $235\text{--}236^\circ$ (decomp.)] and KI in HCl give the *hydriodide*, which forms a MeI compound (II) with excess of MeI and MeOH ($>100^\circ$; 2—4 hr.). Hydroquinidine *methiodide*, m.p. $242\text{--}243^\circ$ (decomp.), *hydriodide* (MeI compound), and MeI compound (impure) are similarly prepared. A. J. E. W.

Reduction studies in the morphine series. IX. Hydroxycodineone. R. E. LUTZ and L. SMALL (J.

Org. Chem., 1939, 4, 220—233).—Thebaine in glacial AcOH is oxidised by 30% H_2O_2 to hydroxycodeinone (I), m.p. 275—276° (vac.), $[\alpha]_D^{25} -111^\circ$ in 10% AcOH [*hydrochloride dihydrate*, m.p. 272—274° (vac.), $[\alpha]_D^{25} -80^\circ$ in H_2O ; *hydriodide* (+1 H_2O), m.p. 255—260° (vac.), $[\alpha]_D^{25} -74^\circ$ in H_2O ; *perchlorate* (+2 H_2O), m.p. 241—242° (decomp.), $[\alpha]_D^{25} -80^\circ$ in H_2O ; Ac derivative, m.p. 185°, $[\alpha]_D^{25} +21^\circ$ in 10% AcOH, and its hydrochloride, m.p. 260—261° (vac.), $[\alpha]_D^{25} +15.7^\circ$ in H_2O]. Reduction (Pd-BaSO₄ in 10% AcOH) of (I) affords dihydrohydroxycodeinone (II), m.p. 218°, $[\alpha]_D^{25} -97^\circ$ in 10% AcOH [*hydrochloride* (+2.5 H_2O), m.p. 270—272° (decomp.), $[\alpha]_D^{25} -123^\circ$ in H_2O], which is not affected by Zn and AcOH at 80—90° and is transformed by Zn-Hg and conc. HCl into dihydrohydroxythebainone, m.p. 143°. Boiling Ac₂O containing NaOAc transforms (II) into *acetoxylidihydrocodeinone enol acetate*, m.p. 207.5°, $[\alpha]_D^{25} -167^\circ$ in EtOH. Zn dust and glacial AcOH at 50—55° convert (I) into hydroxythebainol and hydroxycodeine (+1 H_2O), m.p. 304—305° (vac.), $[\alpha]_D^{25} -143^\circ$ in 10% AcOH [*hydrochloride*, m.p. 269—275° (decomp.)]; the base is reduced (PtO₂ in 10% AcOH) to *dihydrohydroxycodeine-A*, m.p. 301—302° (vac.), $[\alpha]_D^{25} -64^\circ$ in 10% AcOH, which has no phenolic properties and does not give a cryst. Ac₁ or Ac₂ derivative. Hydrogenation (PtO₂ in 10% AcOH) of (II) slowly yields *dihydrohydroxycodeine-B* (III), m.p. 145—145.5°, $[\alpha]_D^{25} -136^\circ$ in 10% AcOH, and -C (IV), m.p. 166—167°, $[\alpha]_D^{25} -152^\circ$ in 10% AcOH. (III) is transformed by Ac₂O and C₅H₅N at 100° into its Ac₂ derivative, m.p. 181—182°, $[\alpha]_D^{25} -127^\circ$ in 10% AcOH [*H tartrate monohydrate*, m.p. 181—182°, $[\alpha]_D^{25} -78^\circ$ in H_2O ($c = 0.72$)]. Excess of MeI at 100° transforms (III) into the *methiodide*, m.p. 223—224° (decomp.), $[\alpha]_D^{25} -87^\circ$ in H_2O , transformed by boiling aq. NaOH into *dihydrohydroxycodeine-B-methine*, m.p. 103°, $[\alpha]_D^{25} -70^\circ$ in 10% AcOH [*H tartrate* (+4 H_2O), m.p. 190—191° (decomp.), $[\alpha]_D^{25} -25^\circ$ in H_2O]; this is hydrogenated (PtO₂ in 75% AcOH) to *dihydrohydroxycodeine-B-dihydromethine*, m.p. 168°, $[\alpha]_D^{25} -44^\circ$ in 10% AcOH [*acetate* (+1.5 H_2O)]. PCl₅ and (III) in CHCl₃ at room temp. yield *dihydrohydroxychlorocodide* (V), m.p. 213.5—214°, $[\alpha]_D^{25} -151^\circ$ in 10% AcOH, which is not reduced by Pt-H₂ in 5% AcOH, or by Clemmensen's method; it is transformed by NaOEt at 140° into liquid phenolic products free from halogen whilst it is indifferent to gentler treatment. SOCl₂ at room temp. converts (III) into *chlorodihydrohydroxycodeine-B* (*hydrochloride*, m.p. 238—239°, $[\alpha]_D^{25} -106^\circ$ in H_2O), which is unaffected by boiling 10% AcOH or by Clemmensen reduction and is converted by Na and abs. EtOH under N₂ into (III). SOCl₂ and (V) give *chlorodihydrohydroxychlorocodide*, m.p. 163.5°, $[\alpha]_D^{25} -141^\circ$ in 10% AcOH, also obtained by use of PCl₅. Reduction of (V) with Na and boiling EtOH affords *dihydrodeoxyhydroxycodeine*, m.p. 137—138°, $[\alpha]_D^{25} -19^\circ$ in 10% AcOH, hydrogenated (PtO₂ in 3% AcOH) to *tetrahydrodeoxyhydroxycodeine* (*perchlorate*, m.p. 242—244°, $[\alpha]_D^{25} -28^\circ$ in H_2O). PCl₅ and (IV) in CHCl₃ give a compound, m.p. 136—139°, which contains P. With SOCl₂ (IV) affords a substance which can be distilled in a high vac. but does not give cryst. derivatives. *Deacetyldihydrohydroxycodeine-C*, m.p. 203°, $[\alpha]_D^{25} -107^\circ$ in 10% AcOH [*H tartrate*

monohydrate, m.p. 209—210°, $[\alpha]_D^{25} -67^\circ$ in H_2O ($c = 0.80$)], does not appear to be isomerised by prolonged treatment with boiling Ac₂O-C₅H₅N.

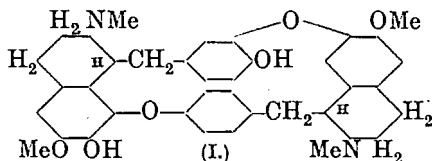
H. W.

Strychnos alkaloids. XXI. Synthesis of isomeric pyrroloquinolines and an isomeride of vomipyrine. L. HORNER (Annalen, 1939, 540, 73—83; cf. A., 1938, II, 514).—6-Amino-8-ethylquinoline, m.p. 89° (yellow hydrochloride), is prepared from *o*-C₆H₄Et.NHAc by way of 4:2:1-NO₂·C₆H₃Et.NH₂, m.p. 58°, and 6-nitro-8-ethylquinoline, m.p. 68° [*hydrochloride*, m.p. 150° (decomp.)], and gives a hydrazone, which with PrⁿCO·CO₂H gives the *hydrazone*, C₁₆H₁₉O₂N₃, m.p. 135°, converted by ZnCl₂ into 8:4'-*diethylpyrrolo-2':3'-6:5-quinoline*, m.p. 142° [*hydrochloride*, m.p. 244° (decomp.)]; not vomipyrine (I). Decarboxylation of the 10-carboxylic acids by molten ZnCl₂ (heating with Cu powder is without effect) yields *pyrrolo-2':3'-5:6-*, m.p. 236—238°, and *-1':2'-8:7-quinoline*, m.p. 94—96°. Absorption spectra are detailed for these and other tricyclic bases containing two nitrogenous rings, and it is concluded therefrom that (I) is a pyrroloquinoline, the position of the substituents remaining, however, uncertain. CHPhMeEt and HNO₃-H₂SO₄ give mixed *o*- and *p*-NO₂-derivatives, reduced to the mixed amines, b.p. 115°/12 mm., which yield an Ac derivative, m.p. 122—124°; with fuming HNO₃ in AcOH this gives *p*-NO₂·C₆H₄.NHAc and *p*-NO₂·C₆H₄.NH₂, and with HNO₃-H₂SO₄ gives *p*-NO₂·C₆H₄.NH₂.

R. S. C.

Curare alkaloids. IV. Bebeerine and tuho-curarine. Orientation of phenolic groups. H. KING (J.C.S., 1939, 1157—1164).—Ethylation (EtI) of the Na salt of bebeerine (I) gives *O*-ethylbebeerine, the methochloride of which on Hofmann degradation in two stages affords *O*-ethylbebeerilene (II), m.p. 168—169°; this is oxidised (KMnO₄) to a mixture of two acids, C₁₈H₁₆O₆.H₂O, m.p. 197° (efferv.), and C₁₈H₁₆O₆.0.5H₂O, m.p. 255°. Diazotised NH₂Ph and *o*-4-xylenol give a mixture of 2-hydroxy-4:5- (III) and 6-hydroxy-2:3-dimethylazobenzene; reduction (Na₂S₂O₃) of the Me derivative of (III) yields NH₂Ph, 5:1:2:4-OMe·C₆H₂Me₂.NH₂, and 4'-amino-3:4-dimethyldiphenylamine, m.p. 114—115° (*monohydrochloride*, m.p. 205°). Nitration, followed by esterification, of 4:1:2-OMe·C₆H₃(CO₂H)₂ (IV) gives some 2-Me 1-H 3-nitro-4-methoxyphthalate, m.p. 186—187°, and 5:4:1:2-NO₂·C₆H₂(OMe)(CO₂Me)₂; reduced (Pd-C-H₂) to Me 5-amino- (V), m.p. 149°, and 5-azoxy-4-methoxyphthalate, m.p. 175—180°. (V) is converted into the corresponding -I-derivative (VI), m.p. 111—112°, which condenses (Cu) with Me isovanillate to give veratric acid, 4-methoxyphthalic acid, and 4:5:5'-tricarboxy-2:2'-dimethoxydiphenyl ether, identical with the compound obtained by degradation and oxidation of *O*-methylbebeerine. Demethylation (HBr) of *O*-ethylvanillic acid affords some protocatechuic acid and 3-hydroxy-4-ethoxybenzoic acid, m.p. 218—219°, the Me ester, m.p. 127—128°, of which condenses with (VI) to give 4:5:5'-tricarboxy-2-methoxy-2'-ethoxydiphenyl ether, m.p. 258—259° [identical with one of the acid oxidation products from (II)], 3:4-

OMe·C₆H₃(OEt)·CO₂H, (IV), and *m*-hemipinic acid. NaOH with Cu (trace) and (VI) yields *O*-methyl-*nor-m*-hemipinic acid, which is brominated to 3-bromo-4-hydroxy-5-methoxyphthalic acid, the Me₂ ester, m.p. 153–154°, of which is ethylated (C₂H₄N₂) to *Me* 3-bromo-5-methoxy-4-ethoxyphthalate, m.p. 83–84° [acid, m.p. 206° (efferv.)]; 1-Et 2-H ester, m.p. 131°. This ester condenses with *p*-OH·C₆H₄·CO₂Me to give anisic acid, 5-methoxy-4-



ethoxyphthalic acid [monohydrate, m.p. 192° (efferv.)], and 5:6:4'-tricarboxy-3-methoxy-2-ethoxydiphenyl ether (+H₂O), m.p. 195° (efferv.), identical with the second oxidation product from (II). These syntheses fix the structure of (I) as shown.

F. R. S.

Constitution of cassaine and partial synthesis of the alkaloid. F. FALTIS and L. HOLZINGER (Ber., 1939, 72, [B], 1443–1450).—Cassaine (I), m.p. 140°, [α]_D²⁰ −104.2° in 96% EtOH, −114.6° in 0.1N-HCl, from *Erythrophleum guineense*, Don., is hydrolysed to cassia acid (II), [α]_D²⁰ −111.6° in COMe₂, allocassaic acid (III), [α]_D²⁰ −109.7° in COMe₂, and NMe₂·[CH₂]₂·Cl. Its partial syntheses from Na cassate (III) and the base in boiling xylene is described. Analogously (III) and NEt₂·[CH₂]₂·Br afford *homocassaine* [diethylaminoethyl cassate], m.p. 107–109° after softening at 106°. Diethylaminoethyl bromide hydrobromide, m.p. 203° (decomp.), is obtained from NEt₂·[CH₂]₂·OH and HBr (saturated at 0°) at 100°. CH₂N₂ and (II) yield *Me* cassate, m.p. 188–189° after softening at 183°, which does not depress the m.p. of the compound obtained similarly from (III). (II) contains one double linking since it is hydrogenated (Pd-sponge in AcOH) to *dihydrocassaic acid* (IV), m.p. 229–235° after softening at 224°, also obtained from (III) [*Me* ester, m.p. 108°, and its *semicarbazone*, m.p. 185–187° (decomp.) after softening at 177°]. CrO₃ in AcOH oxidises (IV) to *dehydrodihydrocassaic acid* C₂₀H₃₀O₄, m.p. 228–229° (decomp.) after softening at 215° (*Me* ester, m.p. 98.5–99°, and its *disemicarbazone*, m.p. 249–250°).

H. W.

Veratrine alkaloids. V. Selenium dehydrogenation of cevine. L. C. CRAIG and W. A. JACOBS (J. Biol. Chem., 1939, 129, 79–87).—Se dehydrogenation of cevine in H₂ yields various volatile products including β-picoline, 5-methyl-2-ethylpyridine, and a base, C₈H₉ON (*picrate*, m.p. 150–151°). The non-volatile products, on chromatographic adsorption in C₆H₆, yield the following: cevanthridine (C₂₃H₂₅N, m.p. 211–212°); unidentified bases possibly homologous with cevanthridine; a base, C₂₅H₂₅N, m.p. 229–230°; a base, C₂₄H₂₅N or C₂₃H₂₃N, m.p. 186°; a hydrocarbon, C₁₇H₁₆, m.p. 138–150°, possibly derived from cevanthrol; a hydrocarbon, C₁₈H₁₈, m.p. 116–118°; and cevanthrol, C₁₇H₁₆O, m.p. 195–196°.

P. G. M.

Alkaloids of *Sinomenium* and *Cocculus*. XLIX. Alkaloids of *Stephania cepharantha*, Hayata. VI. Systematic method of separation of the alkaloids. H. KONDO, M. TOMITA, M. SATOMI, and T. IKEDA (J. Pharm. Soc. Japan, 1938, 58, 276–279).—*iso*Tetrandrine (I) (3 g.) is obtained by crystallisation of the total alkaloids (12 g.) from COMe₂. The residue from the COMe₂ mother-liquors is extracted with aq. HCl and the sol. material separated by KOH and Et₂O into phenolic (A) and non-phenolic (B) (5 g.) fractions. Fractional crystallisation of (B) from COMe₂ and then COMe₂-C₆H₆ gives methylisochondodendrine (0.25 g.), then 3 g. of cepharanthine, m.p. 155° (non-cryst.) as the cryst. adduct, decomp. 103°, with 1C₆H₆ (also + 1PhMe, decomp. 98°), and finally amorphous base. Fractional crystallisation of (A) from C₆H₆ affords a little berbamine (II), m.p. 170° [as adduct, m.p. 127° (decomp.)], with 1.5C₆H₆; also +4H₂O, m.p. 156° (decomp.), [α]_D²⁵ +106.3° in CHCl₃ [diperchlorate, m.p. 278° (decomp.)]; dihydrochloride, m.p. 270° (decomp.); hydrobromide, m.p. 283° (decomp.); hydriodide, m.p. 260–264° (decomp.); methiodide, m.p. 261° (decomp.)], and amorphous base. Methylation (CH₂N₂) of (II) gives (I). H. B.

Sinomenine. XLVI. Constitution of tudaranine. K. GOTO and H. SHISHIDO (Annalen, 1939, 539, 262–265; cf. A., 1937, II, 435).—The structure of tudaranine is proved by synthesis of its *dl-N*-Et derivative Et ether ethiodide (I) and the degradation thereof already announced (A., 1939, II, 189) and now detailed. 2:4:1-NO₂-C₆H₃(OEt)·CH₂·COCl and 2:4:1-(OMe)₂C₆H₃·[CH₂]₂·NH₂ give 2'-nitro-4'-ethoxyphenylacet-β-2:4-dimethoxyphenylethylamide, m.p. 127–128.5°, converted by P₂O₅ in hot PhMe into 1-2'-nitro-4'-ethoxybenzyl-6:7-dimethoxy-3:4-dihydroisoquinoline, m.p. 145–147°, the ethiodide, m.p. 160–162°, of which is reduced by Zn dust in HCl to 1-2'-amino-4-ethoxybenzyl-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinoline, m.p. 116–118°. Diazotisation and treatment with Cu-bronze gives 5:6-dimethoxy-3-ethoxy-N-ethylnoraporphin [hydrobromide, m.p. 246–248°; hydrochloride, m.p. 234–236°; ethiodide = (I)]. R. S. C.

Kurchi alkaloids. II. Extraction of conesine and accompanying bases. A. BERTHO (Arch. Pharm., 1939, 277, 237–237; cf. A., 1933, 728).—The extraction of the following bases is described: conesidine (I), [α]_D²⁵ −63.5° in CHCl₃ [dimethiodide, m.p. 269° (decomp., slow heating)], konkurchine (II), [α]_D²⁵ −43.8° in 96% EtOH [dinitrate (+1.5H₂O), darkens at 180° and then explodes; diperchlorate, decomp. 272° (rapid heating); Ac₃ derivative, m.p. 263° (the derivative reported in A., 1933, 728 was not completely acetylated)], kurchine (A., 1932, 406), a *dilert.* base, [α]_D²⁵ +10.6° in EtOH [diperchlorate, m.p. 250° (decomp.)]; dimethiodide, m.p. 286.5°, and konkurchinine (III), C₂₅H₃₆N₂, a *dilert.* base containing no NMe, m.p. 161°, [α]_D²⁵ −47.0° in EtOH [diperchlorate (+2H₂O), darkens at 260° but does not melt at <330°; dimethiodide, m.p. 255–256° (decomp.)]. Since (III) is decomposed by dil. HNO₃, giving the nitrate of (II), and gives a red colour with fuchsin-SO₂, it probably contains the grouping

$\cdot\text{N}\cdot\text{CH}\cdot[\text{CH}_2]_3\cdot\text{N}\cdot$. Many of these bases, in presence of alkali, or when recrystallised or kept, form mol. associates (also formed from mixed bases); some of these occur in the crude alkaloids, and they yield the unimol. forms when treated with conc. HCl and then aq. NH_3 . (I) gives an amorphous form, m.p. 288–289° or >300°, and (II) gives an associate m.p. 323°, and another, m.p. 335–336°, identical with "kurchenine" (A., 1933, 728). The "norconessine" of Haworth (A., 1932, 406) is probably impure kurchine. The properties of the *Kurchi* alkaloids are summarised.

A. Li.

Constitution of matrine. XXI. Curtius degradation of methyl methylmatrate. E. OCHIAI and K. NODA (J. Pharm. Soc. Japan, 1938, 58, 174–176).—*Methylmethylmatrazide*, m.p. 94° (*CMe*₃ derivative, m.p. 128.5°), from the Me ester and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 100° (bath), is converted by HCl and amyl nitrite in EtOH into a compound, $\text{C}_{16}\text{H}_{28}\text{O}_2\text{N}_2$, b.p. 145°/0.02 mm. (*platinichloride*, decomp. 231°), and by NaNO_2 -aq. HCl into a little *decarbonylmethylmatrine*, m.p. 120°, also obtainable in better yield by the Hofmann degradation. *isopropylidenebenzhydrazide* has m.p. 144.5°.

H. B.

Alkaloid (hydrobromide, m.p. 287°) from Twan Chan Tsao.—See A., 1939, III, 639.

Organoboron-nitrogen compounds. I. Reaction of boron chloride with aniline. R. G. JONES and C. R. KINNEY (J. Amer. Chem. Soc., 1939, 61, 1378–1381).— BCl_3 reacts violently with NH_2Ph , but only very slowly with $\text{NH}_2\text{Ph}\cdot\text{HCl}$. With NH_2Ph (0.8 mol.) in C_6H_6 it gives the additive compound (I), $\text{BCl}_3\cdot\text{NH}_2\text{Ph}$ (not obtained quite pure), m.p. ~100°, decomp. ~120°, which decomposes in moist air and dissociates in boiling C_6H_6 . With NH_2Ph in C_6H_6 , (I) gives a very poor yield of the compound, $\text{BCl}_2\cdot\text{NHPh}\cdot\text{NH}_2\text{Ph}$, decomposed by H_2O to NH_2Ph , HCl, and H_3BO_3 . When NH_2Ph is added to BCl_3 in C_6H_6 at -15° and the mixture first kept at room temp. and then boiled, *trichlorotriphenyltriboron nitride*, $\text{BCl}\langle\text{NPh}\cdot\text{BCl}\rangle\text{NPh}$ (II), sinters at 255–260°, decomp. 265–270°, is obtained (cf. Rideal, A., 1889, 769). With cold H_2O (II) gives *trihydroxytri-phenyltriboron nitride* [as (II) with OH replacing Cl], m.p. indefinite, 95–130°, sol. in aq. NaOH and readily hydrolysed to H_3BO_3 and NH_2Ph . With 5 mols. of NH_2Ph in boiling C_6H_6 , (I) gives *boric trianilide* (III), $\text{B}(\text{NHPh})_3$, m.p. 166–169° (decomp.); softens at 155°, if heated slowly, which gives no additive compound with NH_2Ph , is readily hydrolysed by H_2O , and with dry HCl in C_6H_6 gives (II). $\text{BCl}_2\cdot\text{NHPh}$ is a probable intermediate in formation of (II) by both methods. The "tert. B triethylimine," $\text{B}(\text{NHEt})_3$, of Kraus *et al.* (A., 1931, 77) is renamed (ortho)boric triethylamide, this name and that of (III) showing the relation to H_3BO_3 . BCl_3 and NPhMe_2 in C_6H_6 give the 1:1 additive compound, sinters at 125–130°, molten at 146°, after resolidification remelts at 144–145°, which is stable in C_6H_6 or over P_2O_5 , loses HCl in moist air, reacts with H_2O in C_6H_6 but in H_2O alone forms an unreactive, insol. coating, reacts with MeOH to give NPhMe_2 , Me_3BO_3 , and HCl, and is decomposed by NH_2Ph . Analysis of the products is discussed.

Et_3BO_3 and NH_2Ph do not react, even if boiled (cf. carboxylic esters).

R. S. C.

Preparation and reactions of lead triphenyl derivatives. L. S. FOSTER, W. M. DIX, and I. J. GRUNTFEST (J. Amer. Chem. Soc., 1939, 61, 1685–1687).— PbPh_4 (prep. in >81% yield from PbCl_2 and MgPhBr in boiling xylene) and I in CHCl_3 give PbPh_3I , m.p. 142° (uncorr.), which with Na in liquid NH_3 gives >90% of Pb_2Ph_6 , obtained also in similar yield from PbPh_3Cl by Na_2Pb_0 (not by Na) in NH_3 at -33.4°. Pb_2Ph_6 has an irregular temp. of decomp., is largely dissociated in C_6H_6 , and with Na in NH_3 gives NaPbPh_3 , obtained impure from PbPh_3Cl or PbPh_3I by Na. Existence of PbPh_3^+ in solution in NH_3 is proved by interaction with EtBr to give PbPh_3Et . NaPbPh_3 and NH_4Br in NH_3 give NH_4PbPh_3 (not isolated owing to its solubility), which is ionised in solution (proof: formation of PbPh_3Et) and destroyed only by a large excess of NH_4^+ . Reaction of NaPbPh_3 with CH_2Cl_2 is complex.

R. S. C.

Lead tetraphenyl and lead diphenyl dihalides. W. C. SETZER, R. W. LEEPER, and H. GILMAN (J. Amer. Chem. Soc., 1939, 61, 1609–1610).—Adding PbCl_2 slowly to MgPhBr in $\text{Et}_2\text{O}-\text{PhMe}$ and then heating gives 82–83% of PbPh_4 , m.p. 225–226°, with sometimes, 6% of PbPh_3Br . PbPh_3 and MgBr_2 give PbPh_3Br , but PhPh_4 is unaffected by MgBr_2 or $\text{Mg} + \text{MgBr}_2$. PbPh_3 is thus an intermediate in the prep. of PbPh_4 . Adding PbPh_4 to boiling, conc. HNO_3 gives $\text{PbPh}_2(\text{NO}_3)_2$, which with NaBr or NaI in very dil. HNO_3 gives 96% of PbPh_2Br_2 or 98% of PbPh_2I_2 , respectively. $\text{PbPh}_2(\text{NO}_3)_2$ and conc. HCl give 93% of PbPh_2Cl_2 . PbPh_2I_2 and KF in aq. EtOH give 92% of PbPh_2F_2 , m.p. >300°, which with MgPhBr gives PbPh_4 .

R. S. C.

Ammino-compounds of lead triphenyl chloride. L. S. FOSTER, I. J. GRUNTFEST, and L. A. FLUCK (J. Amer. Chem. Soc., 1939, 61, 1687–1690).—By measuring the vol. of NH_3 absorbed and by isolating the compounds, it is shown that at -33.4° PbCl_2 with NH_3 vapour gives compounds containing 9.65, 2.7, 1.8, or 1.3 mols. of NH_3 . Only the first-mentioned compound was examined in detail.

R. S. C.

Synthesis in the selenophen series. IV. Introduction of side-chains into the selenophen nucleus. S. UMEZAWA (Bull. Chem. Soc. Japan, 1939, 14, 155–161; cf. A., 1937, II, 172).— $\text{C}_4\text{H}_4\text{Se}$ and AcCl with SnCl_4 in C_6H_6 or CS_2 yield α -aceto-selenenone (I), b.p. 107°/14.5 mm. (*phenylhydrazone*, m.p. 114–116°), oxidised (dil. NaOH- KMnO_4) to α -selenenylglyoxylic acid, m.p. 92–94° [*monohydrate*, m.p. 44–46.5°; *semicarbazone*, m.p. 192–193°; *Ba salt* (+ H_2O)], which with H_2O_2 yields α -selenenoic acid (II), m.p. 122–124° (*Ag salt*). α -Chloromercuriselenophen, m.p. 201–202° (from $\text{C}_4\text{H}_4\text{Se}$, NaOAc , and HgCl_2 in aq. EtOH), with EtCOCl at 100° yields α -propioselenenone, b.p. 115°/14 mm. [also prepared as (I)] (*semicarbazone*, m.p. 175–176°), oxidised (dil. NaOH- KMnO_4) to (II). $\text{C}_4\text{H}_4\text{Se}$ and BzCl with P_2O_5 , or with SnCl_4 in CS_2 , give *Ph* α -selenenyl ketone (poor yield), m.p. 57–58° (*phenylhydrazone*, m.p. 175–176.5°). (I) with PhCHO and HCl gas at -10° yields

styryl α-selenenyl ketone, m.p. 81–82.5° (dibromide, m.p. 155.5–156°). These ketones are much more stable than C_4H_4Se . (I) and (II) give the indophenin reaction.

A. Li.

Relative reactivities of organometallic compounds. XXVII. Thallium triphenyl. H. GILMAN and R. G. JONES (J. Amer. Chem. Soc., 1939, **61**, 1513–1515; cf. A., 1939, II, 350).— $TlPh_3$ (prep. from $LiPh$ and $TlPh_2Br$ in 70% yield), m.p. 169–170° (in N_2), is less reactive than AlR_3 , but undergoes some of the reactions of moderately reactive organometallic compounds. It gives the colour test (modified) with Michler's ketone (A., 1925, ii, 1011). With $PhCHO$ in C_6H_6 it gives $CHPh_2OH$ (76%) and $TlPh_2OH$. With $PhNCO$ it gives $NHPhBz$ (40%). With $BzCl$ it gives $COPh_2$ (89%) and $TlPh_2Cl$ (97%). With $COPh \cdot CH \cdot CHPh$ in C_6H_6 it gives $COPh \cdot CH_2 \cdot CHPh_2$ (41%) and $COPh \cdot CH(CHPh_2) \cdot CHPh \cdot CO \cdot COPh$ (30%). With Hg in hot C_6H_6 it gives $HgPh_2$ (45%) (obtained in 90% yield from $TlPh_2Br$ and Hg in hot, dry C_5H_5N). With O_2 in C_6H_6 it gives 11% of $PhOH$ and some Ph_2 . With CO_2 in boiling xylene it gives $BzOH$ (70%) and Ph_2 (73%). It gives oils with $COPh_2$ or CO_2 in C_6H_6 .

R. S. C.

Structure of proteins. L. PAULING and C. NIE-MANN (J. Amer. Chem. Soc., 1939, **61**, 1860–1867).—X-Ray data are shown in a crit. review to be incompatible with the cyclol structure of proteins instead of supporting it as assumed by Wrinch. Bond energy vals. and heats of combustion each show that the cyclol structure would be less stable than the polypeptide chain by about 28 kg.-cal. per mol. of NH_2 -acid, so that at most 3% of the NH_2 -acid residues possess the former structure. Other evidence against the cyclol theory is assembled and accepted, and Wrinch's more important arguments are refuted in detail. Moreover, the necessary overlapping of side-chains at corners and edges, contrasted with the rather uniform distribution of matter revealed by crystal structure analysis, is held to refute all cage structures and not merely Wrinch's particular choice. Proteins are considered to consist of polypeptide chains or rings built up from several hundred NH_2 -acids; small nos. of residues held together by H bonds etc. would be at once disrupted in acid or alkali, which is not the case. The chains are given definite shapes by NH_2 - CO_2H , S-S, and ester linkings, but mainly by H bonds, which latter, although individually weak, are very effective in aggregate. If the structure thus assumed is the most stable possible, denaturation is reversible (trypsin, haemoglobin); if not, denaturation is irreversible, as with antibodies, the initial structure of which is enforced by the antigen during synthesis. The nature of the end-groups is important only for enzymic attack and biological action, but not for structure. Whilst the periodicity proved by Bergmann indicates 288 residues in the mol. of many proteins, this no. will be modified by side-groups or occasional variations in assembly of the residues and will often be only approx. The significance of this no. is not clear. Favoured mol. wts. probably have a biological rather than a chemical cause, viz., retention of this protein property throughout evolution of the species.

R. S. C.

X-Rays and the cyclol hypothesis. J. D. BERNAL, I. FANKUCHEN, and D. RILEY (Nature, 1939, **143**, 897).—A reply to Wrinch (A., 1939, II, 397):

L. S. T.

Casein. III. Fractionation of casein and paracasein by ammonium chloride. IV. Hammarsten's proteose is not a degradation product of casein. E. CHERBULIEZ and J. JEANNERAT (Helv. Chim. Acta, 1939, **22**, 952–959, 959–961).—III. Casein is dissolved in aq. NH_4Cl with the aid of $NaOH$ and fractionally pptd. by HCl and CO_2 ; the process leads essentially to two fractions, casein- α_1 and - γ with a little δ . Each contains a little Ca but the presence of this ion does not influence the result since no difference is observed if $NaOH$ is replaced by $Ca(OH)_2$. Rennet is practically without action on casein- δ and has its max. action on the mixture of - α_1 and - γ , whereas each of the latter separately is only incompletely coagulated. Paracasein is obtained by the action of rennet on a solution of Ca caseinate, whereby it is pptd. as its Ca salt free from casein; elimination of Ca from the ppt. necessitates repeated dissolution and pptn. Alternatively a solution of casein is treated with rennet in the absence of alkaline-earth ions, whereby the product is as free as the original material from Ca but is liable to be contaminated with unchanged casein. Fractionation of paracasein gives essentially α_1 and γ with less δ than is the case with casein.

IV. Hammarsten's proteose is identical with casein- δ in content of P, S, and methionine, in the coloration with CH_2O and HCl in presence of H_2SO_4 , and in physical properties. Proteose is therefore not a degradation product of casein formed under the proteolytic influence of rennet, but a preformed constituent in the mixture, casein.

H. W.

Pantothenic acid. IV. Formation of β-alanine by cleavage. H. H. WEINSTOCK, jun., H. K. MITCHELL, E. F. PRATT, and R. J. WILLIAMS (J. Amer. Chem. Soc., 1939, **61**, 1421–1425; cf. A., 1939, II, 172).—Pantothenic acid is synthesised by yeast only if the medium contains β-alanine, which is shown by quant. chemical, physical, and biological tests to be formed by acid or alkaline degradation of the acid and is isolated from the products as β-naphthalenesulphonyl derivative, m.p. 135.5–136.5°. The acid is probably a protein, ~80% pure, yielding 1 equiv. of β-alanine.

R. S. C.

Eisninin, $C_{13}H_{20}O_6N_4$, m.p. 225–226° (decomp.), $[\alpha]_D^{25} -54.3^\circ$ in H_2O , from *Eisenia bicyclis*.—See A., 1939, III, 733.

Precipitation of proteins with complex salts.—See A., 1939, III, 885.

Organic chemical operations with small amounts of material. J. ERDÖS and B. LÁSZLÓ (Mikrochem., 1939, **27**, 211–215).—A review.

Organic micro-analysis. VII. Improvements to Pregl's micro-analytical apparatus. S. SAKAMOTO (J. Pharm. Soc. Japan, 1938, **58**, 304–306).—An improved CO_2 generator and pressure regulator are described.

S. H. H.

Refractive index measurements in qualitative organic micro-analysis. P. L. KIRK and C. S.

GIBSON (Ind. Eng. Chem. [Anal.], 1939, 11, 403).—A method of measuring n of small quantities of org. liquids is described. For solids immersion methods can be applied when the val. of n is known. Determination of n is a valuable adjunct to the identification of org. compounds. L. S. T.

Handling of hygroscopic substances in the micro-determination of carbon and hydrogen. C. J. RODDEN (Ind. Eng. Chem. [Anal.], 1939, 11, 405).—The apparatus described and illustrated consists of a jacketed drying tube arranged so that it may be kept at a const. temp., and a weighing bottle of special design. The sample is dried, weighed, and introduced into the C and H combustion tube without contact with moisture. L. S. T.

Quantitative organic elementary micro-analysis without a micro-balance. J. B. NIEDERL, V. NIEDERL, R. H. NAGEL, and A. A. BENEDETTI-PICHLER (Ind. Eng. Chem. [Anal.], 1939, 11, 412—414; cf. A., 1939, I, 341).—Micro-procedures with minor changes, such as in the time factors in the C and H determination and in the Dumas N method, can be employed when an assay balance or an ordinary analytical balance of suitable precision is available. Changes in equipment and micro-apparatus are unnecessary. Typical results thus obtained in the determination of metals, neutralisation equiv., N by the Kjeldahl and micro-Dumas methods, C and H, and mol. wt. are recorded. L. S. T.

Detection of nitrogen in the organic laboratory. A. G. EPPRECHT and B. HORNING (Helv. Chim. Acta, 1939, 22, 925—927).—A few mg. of the substance are mixed with CaO in a glass tube >5 mm. in diameter; if NO_2 - or azo-compounds are present a little Cu powder is added. A drop of HCl (1:1) on a Pt or glass loop or placed in filter-paper is brought into the tube, which is moderately heated. The loop of paper is placed in a drop of Riegler's solution to which an excess of CaO is added. If N is present a distinct red colour due to NH_4 is developed in the solution after a short time. A micro-analytical modification of the test is described. H. W.

Semimicro-determination of halogens in organic substances. A. GIACALONE (Annali Chim. Appl., 1939, 29, 271—277).—The substance (~ 50 mg.) is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ - H_2SO_4 (for Br or I) or Ag_2SO_4 - H_2SO_4 (for Cl); Br or Cl liberated is absorbed in aq. H_2O_2 and the HBr or HCl formed is determined gravimetrically as Ag salt. With I, HIO_3 in the (diluted) digestion liquor and the residual CrO_4 are reduced by SO_2 and I is determined gravimetrically as AgI . F. O. H.

"Deflagration" with sodium peroxide as simple analytical process for determination of halogen, sulphur, and other constituents in organic substances. R. KRAUS (Z. anal. Chem., 1939, 117, 243—252).—Deflagration of solid org. substances and certain liquids by quick and short heating with a large excess of Na_2O_2 in a covered Ni crucible by the method detailed gives a quick and complete combustion with relatively little attack on

the crucible, and permits subsequent determinations of halogens, S, and P to be made accurately. Viscous liquids are first mixed with MgO , and liquids of high b.p. are absorbed in filter-paper in the crucible before mixing with the Na_2O_2 . The method is limited for low % of Cl, S, etc. only by the "blank" of the Na_2O_2 . It is applicable to substances, such as chlorotoluidine, which are not readily decomposed by the Carius method. The method is especially suitable for routine analyses. L. S. T.

Organic micro-analysis. IV. Simple volumetric micro-determination of ionisable organic halogen derivatives with adsorption indicators. S. UYEO and S. SAKAMOTO (J. Pharm. Soc. Japan, 1938, 58, 212—218).—Ionisable halogen in org. compounds is determined by dissolving 3—5 mg. of the substance in H_2O or aq. EtOH , adding (for Cl) bromophenol-blue and 10% AcOH or (for Br or I) eosin, and titrating with 0.01—0.002N- AgNO_3 . In 102 examples the error exceeds 0.4% in 9 cases (± 0.2 —0.3% claimed). R. S. C.

Reaction of organic sulphur compounds with hydrogen peroxide. XVII. Gravimetric micro-analysis of organic sulphur compounds. III. R. KITAMURA and F. MASUDA (J. Pharm. Soc. Japan, 1938, 58, 251—254).—S in compounds containing $\text{N}:\text{C}:\text{SH}$, $\text{O}:\text{C}:\text{SH}$, $\text{S}:\text{C}:\text{SH}$, $\text{N}:\text{C}:\text{S}$, $\text{O}:\text{C}:\text{S}$, $\text{S}(\text{C}:\text{N})_2$, or $\text{C}:\text{CS}:\text{C}$ is determined by treating 3—5 mg. with H_2O_2 - KOH at 40° , followed by BaCl_2 , and weighing the BaSO_4 produced. R. S. C.

Micro-determination of dipentadeuterethyl ether.—See A., 1939, III, 804.

Differentiating action of solvents on the strength of acids. I. Potentiometric titration of salts by the displacement method, in differentiating solvents. N. A. IZMAILOV and M. A. BELKOVA (J. Gen. Chem. Russ., 1939, 9, 453—459).—Na salts of carboxylic acids are dissolved in aq. COMe_2 , and the solutions are electro-titrated with HCl . The org. acids thus liberated dissociate to a very small extent only, as compared with aq. solutions, whilst dissociation of HCl is not affected. The $[\text{COMe}_2]$ should be $\leq 85\%$. The method is applicable to all carboxylic acids, including $\text{CCl}_3\text{-CO}_2\text{H}$. R. T.

Accuracy of iodometry for the determination of ascorbic acid; method for standardisation of preparations. K. SHINOHARA (J. Pharm. Soc. Japan, 1938, 58, 279—292).—Ascorbic acid (I) can be determined accurately by titration with 0.01N-I in solutions of p_H 0.7—5 containing KCNS . At $p_H > 6$ and < 9 results are too low [owing to atm. oxidation of (I)] unless titration is carried out in N_2 . Direct titration of (I) in $\leq 0.5\text{M-HCl}$ also gives low results owing to slow reaction; excess of I and back titration with $\text{Na}_2\text{S}_2\text{O}_3$ give moderately accurate vals. Oxidation of dehydroascorbic acid (II) by I is negligible at $p_H < 6$ but occurs at 6—8 and is a max. at 7.4—7.6. Aq. solutions of (I) are more stable [to atm. oxidation to (II)] than those in dil. HCl or H_2SO_4 ; KCNS ($25 \times 10^{-4}\text{M}$) has a pronounced inhibitory effect and is more effective than HPO_3 . The procedure recommended is: (I) (0.1761 ± 0.0001 g.) is dissolved in $25 \times 10^{-4}\text{M-KCNS}$ to 200 c.c. and 5 or

10 c.c. are then titrated with 0.01N-I (in 4% KI) using starch solution as indicator; the error is $< \pm 0.3\%$.

H. B.

Determination of formaldehyde. I. Hydrogen peroxide method. A. FOSCHINI and M. TALENTI (Z. anal. Chem., 1939, 117, 94—99).—Sources of error in the official method of the Italian Pharmacopœia (5th edition) for the determination of CH_2O by H_2O_2 are discussed and methods for their elimination suggested. The CH_2O should be measured by a micro-burette, and the alkaline mixture constantly agitated to facilitate the removal of gases. Contamination by CO_2 from gas-heated water-baths should be avoided by electrical heating. Results thus obtained are more const. and are lower than those obtained by the official method.

L. S. T.

Determination of metaldehyde. SCHONBERG (Ann. Falsif., 1939, 32, 178—181).—Metaldehyde is depolymerised by heating at 65—75° for 1—2 hr. with aq. H_3PO_4 , the MeCHO formed being absorbed in aq. NaHSO_3 and determined iodometrically.

E. C. S.

Identification of ethers. P. P. T. SAH (Rec. trav. chim., 1939, 58, 758—760).—A small sample of the ether is passed through a quartz tube at 500° and the issuing gas passed through a solution of a reagent (*o*- or *p*-tolylsemicarbazide; *m*-nitro- or *p*-chloro-benzhydrazide) by which the aldehyde or ketone is identified and the ether may be deduced. Et_2O gives C_2H_6 and MeCHO ; Pr^nO gives C_3H_8 and EtCHO ; Pr^iO gives C_3H_8 and COMe_2 ; Bu^nO gives C_4H_{10} and Pr^nCHO ; Bu^iO gives C_4H_{10} and Pr^iCHO ; (*sec*- Bu) $_2\text{O}$ gives C_4H_{10} and COMeEt ; $\text{CH}_2\text{Ph}\cdot\text{OEt}$ gives PhMe , C_2H_6 , MeCHO , and PhCHO ; $\text{CH}_2\text{Ph}\cdot\text{OPr}$ gives PhMe , C_3H_8 , EtCHO , and PhCHO ; $\text{CH}_2\text{Ph}\cdot\text{OPr}^i$ gives PhMe , C_3H_8 , COMe_2 , and PhCHO ; $\text{CH}_2\text{Ph}\cdot\text{OBu}^n$ gives PhMe , C_4H_{10} , Pr^nCHO , and PhCHO ; $\text{CH}_2\text{Ph}\cdot\text{OBu}^i$ gives PhMe , C_4H_{10} , Pr^iCHO , and PhCHO ; $(\text{CH}_2\text{Ph})_2\text{O}$ gives PhMe and PhCHO .

J. D. R.

Saccharolactone as reagent for precipitating certain amines. A. C. KURTZ and D. W. WILSON (J. Biol. Chem., 1939, 129, 693—699).—Saccharolactone (I) (deteriorates slowly in EtOH) and the free amine in EtOH at room temp. give NN' -*dimethyl*-, m.p. 188°, -*ethyl*-, m.p. 174°, -*n*-, m.p. 179—181°, and -*iso-propyl*-, m.p. 176—178°, -*n*-, m.p. 178°, and -*iso-butyl*-, m.p. 159°, -*n*-, m.p. 173—174°, and -*iso-amyl*-, m.p. 138°, -*n-heptyl*-, m.p. 174—176°, - β -*hydroxyethyl*-, m.p. 129—130°, -*benzyl*-, m.p. 174—176°, and - β -*phenylethyl-saccharimide*, m.p. 185—186°. Similar derivatives from tyramine and piperidine had m.p. 204° and 191° (darkens $> 140^\circ$), respectively. The derivatives of m.p. $< 174^\circ$ show browning and frothing at the m.p. Some solubilities are recorded. Pptn. of the less sol. saccharimides is more rapid with the more symmetrical amines. NH_2Bu gives almost immediate pptn., NH_2Bu^i after 30 min., and $\text{NH}_2\text{Bu-sec}$. no ppt. $(\text{CH}_2\cdot\text{NH}_2)_2$, putrescine, and cadaverine give an immediate gummy ppt. (I) and $\text{NMe}_4\cdot\text{OH}$, NMe_3 , or NEt_3 give no ppt. Sp. pptn. of saccharimides may be used to determine certain amines in mixtures. Aromatic amines give (slowly) cryst. ppts., e.g., from NH_2Ph , m.p. 204—205° (decomp.); *o*-, m.p. 190—191° (decomp.), and

p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 202—203° (decomp.); xylidine, m.p. 190—191° (decomp.); and benzidine, m.p. 275—280° (decomp.).

A. T. P.

Semimicro-determination of amino-acids. H. R. ING and M. BERGMANN (J. Biol. Chem., 1939, 129, 603—607).—Apparatus for semimicro-determination of NH_2 -acids in proteins by the solubility method (cf. A., 1939, II, 236) is described. The reaction product is filtered by centrifugal means. Experiments are recorded giving results of the determination of glycine by means of Na dioxypyridate and of proline in gelatin by NH_4 rhodanilate.

A. T. P.

Naphthalene-2-sulphonic acid as a reagent for amino-acids. M. BERGMANN and W. H. STEIN (J. Biol. Chem., 1939, 129, 609—618; cf. A., 1939, II, 236).— $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ (I) and *l*-leucine or *l*-phenylalanine (II) in dil. HCl form sparingly sol. salts ("nasylates"), $+\text{H}_2\text{O}$ (III), m.p. 187.5—189° (decomp.) and 232—233° (decomp.), respectively. *l*-Arginine and *l*-histidine afford salts, *B*, 2(I), m.p. 209—211° (decomp.), and 265° (decomp.), respectively, converted by $\text{C}_5\text{H}_5\text{N}\cdot\text{MeOH}$ into the corresponding *mono*-salts, *B*, (I), m.p. 243° (decomp.) and 206—207° (decomp.), respectively, which give the di-salts with strong acids. Commercial leucine is freed from methionine by pptn. as (I) salt and treatment with $\text{C}_5\text{H}_5\text{N}\cdot\text{EtOH}$ at room temp.; it had $[\alpha]_D^{25} + 15.33^\circ$ in 21% HCl . Determination of NH_2 -acids by the solubility method [of their (I) salts] (*loc. cit.*) is illustrated. Acetyl-*l*-phenylalanyl-*l*-glutamic acid and boiling HCl give a solution, which on evaporation to dryness and treatment with (I) gives (III), converted by $\text{C}_5\text{H}_5\text{N}\cdot\text{EtOH}$ at 20° for 2 days into (II), $[\alpha]_D^{25} - 34.6^\circ$ in H_2O . The sparingly sol. (I) salt, m.p. 211—212° (decomp.), of glycyl-*l*-leucine can be used for its determination. Tryptophan, methionine, and cysteine give salts with (I). Flavianic acid forms sparingly sol. salts with leucine, phenylalanine, tyrosine, cystine, and tryptophan. NH_2 -acid salts can also be obtained from β -naphtholazobenzene-*p*-sulphonic acid, 4-nitro-4'-methyldiphenylamine-3-sulphonic acid, and anthraquinone-2-sulphonic acid.

A. T. P.

Determination of glutamic acid. A. A. ARHIMO and T. LAINE (Suomen Kem., 1939, 12, B, 18).—The acid is oxidised (HNO_2) to α -hydroxyglutaric acid and finally (acid KMnO_4) to succinic acid, which is extracted with Et_2O and determined by titration of the Ag salt with 0.1N- or 0.005N- NH_4CNS (cf. Cohen, A., 1939, III, 639).

F. O. H.

Volumetric determination of thiocarbamide. C. MAHR (Z. anal. Chem. 1939, 117, 91—94).—The solution of $\text{CS}(\text{NH}_2)_2$ is titrated at 35° with 0.1N- BrO_3^- -Br in presence of acid (H_2SO_4 , HCl , or HClO_4), KI, and starch. The formation of a stable blue colour shows when oxidation to the corresponding $\cdot\text{S}\cdot\text{S}\cdot$ compound is complete. Cu and Hg salts, but not small $[\text{NO}_3^-]$, interfere. H_3PO_4 must be added when Fe^{III} salts are present.

L. S. T.

Effects of methionine, djenkolic acid, and benzylcysteine on the determination of cystine by the dropping mercury electrode. E. R. SMITH and C. J. RODDEN (J. Res. Nat. Bur. Stand., 1939, 22,

669—672).—The polarographic determination of cystine in a buffered solution containing Co^{++} is unaffected by the presence of methionine or benzylcysteine at concns. up to \sim twice the concn. of cystine. Djenkolic acid, however, reduces the height of the reduction max. of cystine. W. R. A.

Determination of arginine in the presence of other amino-acids by means of the Sakaguchi reaction. L. E. THOMAS, J. K. INGALLS, and J. M. LUCK (J. Biol. Chem., 1939, **129**, 263—271).—The Sakaguchi method of determining arginine is further modified so as to be applicable in presence of NH_4 salts and other NH_2 -acids. The colour is always fugitive (cf. lit.). The following arginine contents are determined: casein 3.37—4.12, edestin 16.01—17.01, total protein of liver, plasma, and serum of the dog 5.86, 5.59, and 4.51, respectively, globulin II (dog) 5.93—6.76, insulin 3.31, and protamine 68.3%.

R. S. C.

Titrimetric modification of the glyoxalase method for the determination of reduced glutathione. E. F. SCHROEDER and G. E. WOODWARD (J. Biol. Chem., 1939, **129**, 283—294).—Reduced glutathione is determined by its accelerating effect on the conversion of AcCHO into lactic acid by glyoxalase. The amount of unchanged AcCHO is determined by a modification of the H sulphite method of Clift and Cook (cf. A., 1933, 491). E. M. W.

Drop detection of diazotisable amines. S. I. BURMISTROV (Prom. Org. Chim., 1939, **6**, 328).—A no. of aromatic amines are identified from the colour developing after diazotisation and coupling with $\text{NHPH}\cdot\text{C}_{10}\text{H}_7\cdot\text{x}$. R. T.

Micro-determination of phenols by the "volume-colorimetric" method. A. IONESCO-MATIU, C. POPESCO, and A. POPESCO (J. Pharm. Chim., 1939, [viii], **30**, 49—58).—The method, involving titration of the sol. blue compounds formed from phenols and phosphotungstic acid with $\text{K}_3\text{Fe}(\text{CN})_6$, has been successfully applied to *o*- and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$, pyrogallol, gallic acid, and the tannins. H. G. R.

Colour reaction for the detection and determination of small quantities of β -naphthol. J. A. GAUTIER (J. Pharm. Chim., 1939, [viii], **30**, 70—76).—The method described utilises the colour reaction with NaNO_2 and HCl and will detect 10 μg . of β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ per c.c. H. G. R.

Colour reaction for polyhydric phenols. J. B. ASCHKINAZI (J. Appl. Chem. Russ., 1939, **12**, 309—312).— NaOEt in EtOH is added to the substance, and the solution is shaken with air. Under these conditions polyhydric phenols give the following colorations: *o*- $\text{C}_6\text{H}_4(\text{OH})_2$ grass-green, changing to dull green, 1:3:4- $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$ blue, changing to red, 1:2:3- $\text{C}_6\text{H}_3(\text{OH})_3$ red, changing through brown to violet, 1:2:3- $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{OMe}$ green, changing through blue to violet, gallic acid a white, changing to ultramarine, ppt., *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ olive-green, orcinol rose-red, changing to cerise, phloroglucinol bluish-violet, quinol orange. Guaiacol, veratrole, safrole, isosafrole, piperonaldehyde, mono- and di-ethers of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{OH})_2$, vanillin, 1:2:3- $\text{C}_6\text{H}_3(\text{OMe})_3$, 1:2:6- $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})_2$, and mono-

hydric phenols give no colorations under the above conditions. R. T.

Colour reactions of lignin and tannins. W. G. CAMPBELL and J. C. MCGOWAN (Nature, 1939, **143**, 1022).—The Mitchell colour reaction of gallotannins (A., 1923, ii, 188) and the Cl_2 - Na_2SO_3 reaction of hardwood lignin (B., 1937, 1057) are essentially similar. With lignin, reactions showing the importance of removing excess Cl_2 while the system is still acid and then rendering the solution weakly alkaline for the colour development are described. L. S. T.

Reactions between thiophen and calcium hypochlorite solutions.—See A., 1939, **1**, 476.

Colorimetric determination of pyrrole with isatin and the application of the method to biological materials. G. H. GUEST and W. D. McFARLANE (Canad. J. Res., 1939, **17**, B, 133—138).—Fromm's method (A., 1935, 998) is modified and applied to the determination of pyrrole (I) produced by the dry distillation of proteinaceous substances. The (I) (yield increased by addition of Na_2O_2) obtained from gelatin (II) is derived entirely from proline (III) and hydroxyproline. CuSO_4 catalyses the oxidation of (III) to (I) by Na_2O_2 . (I) is absent from the hydrolysates of (II), gliadin, and glutenin. S. H. H.

Bromometric determination of antipyrine. V. MADIS (Österr. Chem.-Ztg., 1939, **42**, 290—293).—Antipyrine is determined in 0.4N-HCl containing KBr and 0.1% AuCl_3 (1 c.c.; indicator) by titrating with KBrO_3 (2 Br added). Aminopyrine, quinine salts, and codeine salts interfere, but *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, NHAcPh , caffeine, or phenacetin do not. The method is adapted for micro-quant. work. R. S. C.

Alkaloids and their reagents. C. C. FULTON (Amer. J. Pharm., 1939, **3**, 184—192).—A new systematic classification of some 100 reagents in use for identification of alkaloids is proposed, and a table is given showing them in the order of their pptg. power. Phosphomolybdic acid forms a convenient standard for dil. solutions. P. G. M.

Micro-electrophotometric determination of morphine. R. CAHEN and H. FEUER (Compt. rend., 1939, **208**, 1907—1910; cf. A., 1911, ii, 79; 1915, ii, 76).—The solution containing morphine (0.02—0.20 mg.) is evaporated to dryness and the residue treated with pure H_2SO_4 (2.4 c.c.) in a boiling water-bath for 2 min. After cooling, saturated aq. NaOAc (5 c.c.) and 4% HgCl_2 (2 drops) are added; the mixture is boiled, cooled, made up to 10 c.c., and the emerald-green colour determined electrophotometrically (red, neutral, or green filter). The red and grey filters give a 1—5%; and the green a 5—10% error. J. L. D.

Detection of ergotamine and ergotamine in gynergen. A. KOFLER (Angew. Chem., 1939, **52**, 251—253; cf. A., 1937, II, 393; 1938, II, 164; L. Kofler, A., 1939, II, 43).—The microscopical detection method is extended; Et_2O and then CHCl_3 (from NaHCO_3 mixture) extracts (also by intermediate Al_2O_3 adsorption) afford crystals of ergotamine and ergotamine (hydrated), respectively. A. T. P.

A., II.—Organic Chemistry

OCTOBER, 1939.

Direct hydrogenations in presence of nickel. P. SABATIER (Bull. Soc. chim., 1939, [v], 6, 1261—1268).—A lecture.

New catalytic syntheses of hydrocarbons. V. N. IPATIEV (Chim. et Ind., 1939, 42, 215—222).—A lecture.

Hydrocarbon chemistry. E. K. RIDEAL (Trans. Faraday Soc., 1939, 35, 806—810).—An introduction to a discussion dealing with the application of differing interpretations of chain reactions in the thermal decomp., catalytic reactions, technical synthesis, and polymerisation of hydrocarbons. F. R. G.

Existence of methylene in hydrocarbon reactions. R. F. BARROW, T. G. PEARSON, and R. H. PURCELL (Trans. Faraday Soc., 1939, 35, 880—889).—A survey of the literature from which it is concluded that CH_2 has been isolated and exists as an intermediate in numerous reactions. From a qual. consideration of the reactions by which CH_2 may be removed, its rapid disappearance in systems containing H_2 or hydrocarbons becomes readily comprehensible. F. R. G.

Stability of hydrocarbon diradicals and their reactions. C. E. H. BAWN and J. MILSTED (Trans. Faraday Soc., 1939, 35, 889—896).— CH_2 from CH_2Br_2 and Na with H_2 yields mainly CH_4 with a little C_2H_4 . $[\text{CH}_2]_n\text{Br}_2$ ($n = 3, 4, 5$, or 6) with Na in N_2 gives $[\text{CH}_2]_n$ as free radicals having a min. stability at $n = 4$. No evidence for the existence of CHMe could be obtained. F. R. G.

Pyrolysis of two-carbon and three-carbon paraffin and olefine hydrocarbons. I. Equilibrium mixtures. M. W. TRAVERS. II. Pure ethane. III. Influence of nitric oxide on the secondary decomposition of ethane. M. W. TRAVERS and J. A. HAWKES (Trans. Faraday Soc., 1939, 35, 860—864, 864—866, 866—868).—I. Results already recorded (A., 1937, I, 366) are discussed.

II. The thermal decomp. of C_2H_6 at 590° has been repeated with elimination of thermal lag and detailed results are recorded, but the surface influence makes consistent vals. difficult to obtain. The secondary decomp. (formation of CH_4 and aromatic condensate) does not begin until C_2H_4 and H_2 are produced by the primary reaction in accordance with earlier conclusions (*loc. cit.*). Contrary to Storch and Kassel (A., 1937, I, 466), the decomp. products contained $<0.4\%$ of C_3H_8 and C_4H_{10} .

III. The secondary decomp. of C_2H_6 ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{condensation products}$) at 590° is not inhibited by NO . It is concluded that, contrary to Hinshelwood and Staveley (A., 1939, I, 30), free

radicals are not involved in the primary decomp. of C_2H_6 ($\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$). F. R. G.

Reaction of hydrogen atoms with propane and the mechanism of the paraffin decompositions. E. W. R. STEACIE and N. A. D. PARLEE (Trans. Faraday Soc., 1939, 35, 854—860).— $\text{C}_3\text{H}_8 + \text{H}$ at 30° gives exclusively CH_4 but at higher temp. up to 250° increasing amounts of C_2H_6 and C_2H_4 . It is concluded that the reactions $\text{H} + \text{C}_2\text{H}_5 = 2\text{CH}_3$ and $\text{H} + \text{C}_3\text{H}_7 = \text{C}_2\text{H}_5 + \text{CH}_3$ occur readily at room temp. F. R. G.

Preparation of pure gases and of pentane for cryostats.—See A., 1939, I, 484.

Mechanism of catalytic dehydrogenation and cyclisation. R. C. PITKETHLY and H. STEINER (Trans. Faraday Soc., 1939, 35, 979—984).—Treatment of $n\text{-C}_7\text{H}_{16}$ with a dehydrogenating catalyst at 475° leads to the formation of heptene (I) and PhMe ; *cyclo*-paraffins or -olefines are not produced. The evidence points to the formation of (I) as an intermediate rather than a by-product. A mechanism is suggested. F. L. U.

Aromatisation of heptane, heptene, and hexene isomerides on chromic oxide.—See A., 1939, I, 479.

Destructive hydrogenation and destruction of hexadecane. H. I. WATERMAN and J. J. LEENDERTSE (Trans. Faraday Soc., 1939, 35, 985—992; cf. B., 1939, 347).— $\text{C}_{16}\text{H}_{34}$, heated for 1 hr. at 435° with H_2 in contact with Ni on kieselguhr or with Cr_2O_3 , yields mainly *n*-paraffins of mol. wt. $<$ that of $\text{C}_{16}\text{H}_{34}$. Formation of branched chains, cyclisation, and polymerisation also occur as the result of secondary reactions. The yield of CH_4 is large compared with that of other gaseous products. The main reaction is considered to be cracking of the $\text{C}_{16}\text{H}_{34}$ followed by rapid hydrogenation of the destruction products. F. L. U.

Isomerisation of alkenes on alumina and thoria.—See A., 1939, I, 478.

Olefine-isoparaffin additive reactions. S. F. BIRCH and A. E. DUNSTAN (Trans. Faraday Soc., 1939, 35, 1013—1020).—Problems connected with this reaction, experimental details of which have been described (B., 1938, 1007), are discussed, and a reaction scheme is proposed. F. L. U.

Mechanism of catalytic exchange reactions between deuterium and olefines. G. H. TWIGG (Trans. Faraday Soc., 1939, 35, 934—940).—The associative mechanism of Horiuti and Polanyi (A., 1935, 44) for the exchange between C_2H_4 and D

at a Ni catalyst is preferred to the dissociative mechanism of Farkas and Farkas (A., 1938, I, 149). Energies of activation for exchange and hydrogenation, recorded over the range 55—120° for C_2H_4 , $CH_2:CHMe$, $CHMe:CHMe$, and $CH_2:CMc_2$ decrease considerably with increasing mol. wt. of the olefine, although the abs. rates of reaction are similar. However, the abs. vals. of the exchange/hydrogenation ratios are in the order expected from the energy vals. and it is concluded that all the reactions take place on a uniform type of catalytically active centre.

F. R. G.

Polymerisation of hydrocarbons. M. W. PERRIN (Trans. Faraday Soc., 1939, 35, 1062—1067).—A short survey of conditions of polymerisation and of the relation between properties and structure of polymerised hydrocarbons.

F. L. U.

Dimerisation of petroleum hydrocarbons. W. J. SPARKS, R. ROSEN, and P. K. FROLICH (Trans. Faraday Soc., 1939, 35, 1040—1052).—Proposed mechanisms are discussed. Most of the products of the dimerisation of C_2H_4 , $CH_2:CHMe$, $CH_2:CMc_2$, $CHMe:CHMe$, allene and its derivatives, C_2H_2 , and $CH:C:CH:CH_2$ can be explained by an $\alpha\gamma$ rearrangement of a H atom.

F. L. U.

Isomeric transformation of *n*-hexene into β -methyl- Δ^3 -pentene. A. D. PETROV and V. SCHUKIN (J. Gen. Chem. Russ., 1939, 9, 506—508).— Δ^4 -Hexene heated at 325—350° with H_3PO_4 on pumice yields $CMc_2:CHEt$.

R. T.

Peroxides from open-chain olefines and from olefines of a technical cracked benzene. H. HOCK and A. NEUWIRTH (Ber., 1939, 72, [B], 1562—1568).—Prolonged exposure of warm and irradiated Δ^4 -*n*-hexene to O_2 gives very small yields of γ - Δ^4 -*n*-hexenyl H peroxide (I), b.p. 35°/0.2 mm.; the yields are increased by the addition of small amounts of cyclohexene, active C, or fuller's earth and particularly by the salts of heavy metals, e.g., anhyd. $FeCl_3$ or $CuCl$. 30% Na_2SO_3 reduces (I) to Δ^4 -hexen- γ -ol, b.p. 28—30°/1 mm. The mixture of olefines obtained by passing β -methylpentan- α -ol over Al_2O_3 at ~250° gives a better yield of peroxides (not investigated), probably owing to the presence of branched chains. Autoxidation of olefines in a technical cracked benzene from petroleum occurs in the fractions of b.p. ~60—130° but not in those b.p. ~140°. The original material therefore contains inhibitors of peroxide formation. The product contains three well-defined peroxides, b.p. 43°/0.5 mm., 47—50°/0.4 mm., and 54—55°/0.4 mm., respectively, derived from the mono-olefines C_6H_{10} , C_7H_{12} , and C_8H_{14} . Probably also the peroxide corresponding with C_9H_{16} is formed. The peroxides are reduced by Na_2SO_3 to the corresponding alcohols, $C_6H_{10}O$, b.p. 25—26.5°/0.5 mm., $C_7H_{12}O$, b.p. 29.5—30°/0.2 mm., $C_8H_{14}O$, b.p. 53°/0.2 mm., and $C_9H_{16}O$, b.p. 60—65°/0.2 mm. The cyclic nature of peroxides and alcohols is established by their analytical data. Determinations of the parachors indicate that the peroxides are derived from a cyclopentene, cyclohexene, and cycloheptene ring with a Me substituent in an undecided position.

H. W.

Low-molecular polymerisation of dienes and trienes. E. H. FARMER (Trans. Faraday Soc., 1939, 35, 1034—1040).—Recent experimental work by the author and others (cf. A., 1937, II, 395; 1938, II, 79) is reviewed and discussed.

F. L. U.

Butadiene polymerides: elucidation of structure by ozonolysis. R. HILL, J. R. LEWIS, and J. L. SIMONSEN (Trans. Faraday Soc., 1939, 35, 1067—1073).—Ozonolysis of a butadiene (I) polymeride obtained from (I) in aq. emulsion without a catalyst gives $(CH_2:CO_2H)_2$, butane- $\alpha\beta$ -tricarboxylic acid, and resinous acids. Hence (I) under these conditions polymerises by all the possible additive mechanisms; it shows a greater disposition to $\alpha\delta$ addition than when polymerised with Na.

F. L. U.

Butadiene co-polymerides: elucidation of structure by ozonolysis. R. HILL, J. R. LEWIS, and J. L. SIMONSEN (Trans. Faraday Soc., 1939, 35, 1073—1079).—Polymerisation of an equimol. mixture of butadiene (I) with $CH_2:CMc:CO_2Me$ (II) in aq. emulsion gives a C_6H_6 -sol. rubber-like product which is essentially linear. The major product of ozonolysis is β -methylbutane- $\alpha\beta$ -tricarboxylic acid, with smaller amounts of $(CH_2:CO_2H)_2$, $C_8H_{14}(CO_2H)_4$, and a more complex product; > half the polymeride is composed of alternate units of (I) and (II), (I) polymerising mainly by $\alpha\delta$ addition. There are also sections where 2, and others where 3 or more, (II) units are adjacent to one another. Contiguity of (I) units is comparatively rare. A theory of the reaction is proposed which correlates the differences in structure and properties between the co-polymeride and the (I) polymeride (cf. preceding abstract) prepared under comparable conditions.

F. L. U.

Homogeneous catalytic formation of mono- and di-vinylacetylene from acetylene.—See A., 1939, I, 478.

Chemical properties of tetranitromethane, and its probable constitution. C. KRAUZ and J. ŠTEPÁNEK (Chem. Obzor, 1936, 11, 153—155; Chem. Zentr., 1937, i, 1923; cf. A., 1937, II, 43).— $C(NO_2)_4$ has m.p. 13°, b.p. 126°. Its reactions indicate the constitution $(NO_2)_2C:NO\cdot O\cdot NO$.

A. J. E. W.

Controlled sulphochromic oxidation of organic compounds containing oxygen. M. POLONOVSKI and A. LINDENBERG (Compt. rend., 1939, 209, 46—47; cf. A., 1924, i, 364).— $0.02N\cdot K_2Cr_2O_7$ in cold 20% H_2SO_4 does not react with $EtCO_2H$, Pr^iCO_2H , or Bu^iCO_2H but oxidises $CH_3Alk\cdot OH$ and $AlkCHO$ to acids. The amount of $K_2Cr_2O_7$ used indicates that the C chain suffers some oxidation before the fatty acids are formed.

J. L. D.

Alcohols $C_8H_{14(16)}O$ and $C_{10}H_{18(20)}O$ from *Thesium virgatum*.—See A., 1939, III, 884.

Partially methylated hexitols. II. Synthesis of $\alpha\beta\gamma\epsilon\zeta$ -pentamethylidulcitol. R. S. TRIPSON and P. A. LEVENE (J. Biol. Chem., 1939, 129, 575—585; cf. A., 1939, II, 137).—Methylgalactofuranoside and Me_2SO_4 -aq. $NaOH\cdot COMe_2$, then Purdie's reagents, give tetramethylmethylgalactofuranoside (I), b.p. 89°/0.5 mm. (first fractionation gives a mixture of α - and β -forms), containing some tetramethylmethyl-

galactopyranoside (II); its rate of hydrolysis by 0.1N-HCl at 100° is determined. Hydrolysis of (I) gives tetramethyl-*d*-galactofuranose (III) and some (II). No "autocondensation" to octamethyldigalactose was noted. Hydrogenation (Raney Ni) of (III) in H₂O gives $\alpha\beta\delta\epsilon$ -tetramethyldulcitol (IV), m.p. 83–84°, $[\alpha]_D^{25}$ –26.8° in H₂O, also obtained from (I) without isolating (III). (IV) and CPh₃Cl–C₅H₅N at room temp. for 7 days (no moisture) afford ζ -triphenylmethyl- $\alpha\beta\delta\epsilon$ -tetramethyldulcitol, converted into its γ -benzoate, and thence by boiling 80% aq. AcOH into $\alpha\beta\delta\epsilon$ -tetramethyldulcitol γ -benzoate (V), b.p. 167–169°/0.25 mm., $[\alpha]_D^{25}$ –1.2° in COMe₂, and some Bz₂ derivative, b.p. 183°/0.1 mm., $[\alpha]_D^{25}$ –22.1° in COMe₂. Methylation (MeI–Ag₂O) of (V) gives $\alpha\beta\gamma\epsilon\zeta$ -pentamethyldulcitol γ -benzoate, b.p. 142°/0.1 mm., $[\alpha]_D^{25}$ \pm 0.5° in COMe₂, hydrolysed by Ba(OH)₂–aq. EtOH to $\alpha\beta\gamma\epsilon\zeta$ -pentamethyldulcitol, m.p. 23.5°, b.p. 93°/2 mm., $[\alpha]_D^{25}$ –17.1° in EtOH. A. T. P.

Chemical and biochemical hydrolysis of diose phosphate. Analytical applications. P. FLEURY and J. COURTOIS (Compt. rend., 1939, 209, 219–221).—0.1N- α -Glycerophosphate (I) with 0.05N-HIO₄ gives phosphoglycollaldehyde (II), which is hydrolysed (2N-H₂SO₄ at 100°/12 min.) 600 times as rapidly as unoxidised (I). (II) is hydrolysed (N-NaOH at 100° or 37°) to give about 50% of the free PO₄''' theoretically obtainable. (II) when hydrolysed by H₂SO₄ or the phosphatase of sweet almonds at about p_H 5.5 gives H₃PO₄ and an aldehyde, oxidised (HIO₄) to CH₂O and HCO₂H. Both (II) and its hydrolytic product obtained at room temp. show equal reducing properties. (I) and the β -form are in equilibrium in solution (cf. Bailly, A., 1938, II, 353), and as (I) is rapidly oxidised by HIO₄ (cf. Fleury and Paris, A., 1933, 696), and (II) is readily hydrolysed by acid, either (I) or (II) can be determined. J. L. D.

Ring structure in certain aliphatic organic compounds. H. A. SMITH and J. P. McREYNOLDS (J. Amer. Chem. Soc., 1939, 61, 1963–1970).—Ring formation, similar to that postulated to explain the effect of the alkyl chain length of *n*-aliphatic acids on the velocity of esterification in MeOH (A., 1939, I, 206, 376), gives a satisfactory explanation of the effect of the character of an alkyl side-chain on the processes of esterification and hydrolysis, on acid dissociation consts., and on optical activity. The ortho-effect is attributed to the same type of structure.

W. R. A.

Recognition of carboxylic acids as ureides with aid of carbodi-imides. IV. Detection of $\alpha\beta$ -substituted acids. F. ZETSCHE and G. RÖTTGER (Ber., 1939, 72, [B], 1599–1612).—*N*-Acyl-*NN'*-di-*p*-dimethylaminophenylcarbamides (I) are darkest when derived from CHR:CH·CO₂H, somewhat paler if obtained from CRR':CH·CO₂H, and so little coloured if derived from CHR:CR'·CO₂H or CH₂:CR'·CO₂H (α -effect) that the limit of visibility is often not reached. The following (I) are described in which the acyl group is: *acrylyl*, m.p. 144.5° after softening at 141°; α -*crotonyl*, m.p. 150° (corr.); Δ^1 -*hexenoyl*, m.p. 139° (softens at 137°); Δ^2 -*octadecenoyl*, m.p. 115° (softens at 113°); Δ^2 -*hentriacontenoyl*, m.p. 103–104°; *cyclohexylideneacetyl*,

m.p. 151° (softens at 149°); *sorbyl*, yellow form, m.p. 147° (softens at 145°), and orange variety passing into yellow form at 100°; *geranyl*, m.p. 126–127°; *fumaryl*, m.p. 168° (slight decomp.) (softens at 166°); *cinnamoyl*, m.p. 155.5° (softens at 153°); *furfuracrylyl*, m.p. 153–154° (corr.); *piperyl*, m.p. 154° (softens at 153°), re-solidifying at 155° and again melting at ~185°; *acetylenecarboxyl*, m.p. 132° (softens at 129°); *phenylpropionyl*, m.p. 151° (softens at 149°); Δ^2 -*hexenoyl*, m.p. 146° (corr.) (softens at 144°); γ -*phenyl*- Δ^2 -*butenoyl*, m.p. 150–152°; Δ^2 -*butene*- $\alpha\delta$ -*dicarboxyl*, m.p. 210°; Δ^2 -*pentenoyl*, m.p. 148–149° (corr.); *cis*- Δ^2 -*tetracosenoyl*, m.p. 96–97°; *trans*- Δ^2 -*tetracosenoyl*, m.p. 110–111.5°; α -*cyclogeranyl*, m.p. 142–143°; *chaulmoogryl*, m.p. 116.5° (softens at 115°); α -*methylacrylyl*, m.p. 143.5° (softens at 140°); *tiglyl*, m.p. 137° (softens at 135°); *atropyl*, m.p. 134–135°; α -*methylcinnamoyl*, m.p. 139° (softens at 135°); α -*phenylcinnamoyl*, m.p. 152.5° (softens at 151°); $\Delta^{1:4}$ -*dihydrobenzoyl*, m.p. 148–149° (decomp.); *benzoyl*, m.p. between 198° and 218° according to rate of heating; *p-toluoyl*, m.p. 147–148°; *anisoyl*, m.p. 151–153°; *piperonoyl*, m.p. 135–136°; β -*phenylpropionyl*, m.p. 155–156°; *terephthalyl*, becomes discoloured at ~180°, darkens at 200°, softens at ~240°, and decomposes at 320°, which passes in boiling *sec*.-C₈H₁₇·OH into *terephthalyl*-*p*-*dimethylaminophenylimide*, decomp. 340°; *isophthalyl*, m.p. 205–215° (decomp.) (softens at 162° and becomes hard again at ~190°), whence *isophthalyl*-*p*-*dimethylaminophenylimide*, m.p. 244–247° (decomp.) (softens at ~240°); 1-, m.p. 162° (decomp.), and 2-, m.p. 185–190°, *naphthoyl*; *anthracene-9-carboxyl*, m.p. 180° (softens at 177°); 9:10-*dihydroanthracene-9-carboxyl*, m.p. 119–121°; *diphenylacetyl*, m.p. 154–155° and ~180° after resolidification; 2':4'-*dimethoxybenzophenone-2-carboxyl*, m.p. 154–155.5°; β -1-*pyrenoylpropionyl*; γ -1-*pyrenylbutyryl*, m.p. 153–155°; *uran-2-carboxyl*, m.p. 141° (softens at 136°); *thiophen-2-carboxyl*, m.p. 136.5–137°; *nicotinoyl*, m.p. 150° (softens at 128°); *pyridine-2-carboxyl*, m.p. 154° (softens at 150°); *cianoacetyl*, m.p. 262° (softens at 255°).

H. W.

Trifluoroacetates.—See A., 1939, I, 482.

Electrolysis of potassium tiglate. A. D. PETROV and D. A. VJACHIREV (J. Gen. Chem. Russ., 1939, 9, 513–515).—Electrolysis of K tiglate gives (CHMe)₂ and α -methyl- Δ^2 -propenyl tiglate, b.p. 170–195°. 74% of the current is used for the reaction of oxidation of tiglic acid to CO₂ and H₂O. R. T.

Polymerisation of styrene and methyl methacrylate.—See A., 1939, I, 479.

Re-esterification of stearic acid esters with higher fatty acids and re-esterification of tristearin with triolein. Y. TOYAMA (J. Soc. Chem. Ind. Japan, 1939, 42, 218B).—Heating an equimol. mixture of Me stearate (I) with oleic acid (II) at 280 \pm 5° for 2 hr. caused re-esterification and the conversion of 40% of (II) into Me oleate. With (I) and lauric acid, about 30–40% of each constituent reacted analogously. Similarly, considerable re-esterification (30–50%) occurred with mixtures of tristearin (1 mol.) with (II) (3 mols.) or with (II) and

behenic acid. Mixed glycerides were produced by heating an equimol. mixture of tristearin and triolein. E. L.

Acetylation of *θ*-dihydrostearic acids, and diastereoisomeric transformations of these acids when treated with acetic anhydride. V. I. ESAFOV (J. Gen. Chem. Russ., 1939, 9, 503—505).—The isomeride of m.p. 95° is more difficult to acetylate (with Ac_2O) than is that of m.p. 132°, thus confirming the supposition that the OH of the former isomeride are in corresponding positions. The products are in both cases mixtures of the acetates of the two forms. R. T.

Electrolysis of acid-ester salts in non-aqueous solutions, and mechanism of the Crum-Brown-Walker synthesis.—See A., 1939, I, 480.

Separation of [constituents of] mixtures of dicarboxylic acids. F. RENNAMP (Z. physiol. Chem., 1939, 260, 276—278; cf. Klenk, A., 1936, 1225).—A mixture of azelaic and sebacic acid is esterified with $\text{MeOH} + \text{H}_2\text{SO}_4$, the mixture is fractionally distilled at 125—140°/0.01—0.02 mm., the fractions are hydrolysed with KOH in MeOH, the K salts are converted into free acids, and these are crystallised from MeOH. W. McC.

Polarometric study of the action of heat on aqueous solutions of *l*-malic acid. R. DESCHAMPS (Bull. Soc. chim. Belg., 1939, 48, 201—228).—Owing to the formation of dehydration products the *l*-rotation of dil. solutions of *l*-malic acid (I) and the *d*-rotation of conc. solutions each change when the solutions are kept at 75°. The rotations gradually approach new const. vals. characteristic for each concn. Conflicting optical data recorded in the literature for solutions of (I) are attributed to the difficulty of separating the acid from optically active dehydration products. The sign of the rotation of the solutions is reversed within the concn. range 29.5—30.5 wt.-%. The Darbais rule appears to apply to the solutions investigated. J. W. S.

Molecular and electronic effects of substituent on optical activity of tartaric acid. See A., 1939, I, 357.

Infra-red absorption spectra of acetaldehyde, paraldehyde, α - and β -trithioacetaldehyde.—See A., 1939, I, 402.

Raman spectra of α - and β -trithioacetaldehyde and of monothioparaldehyde.—See A., 1939, I, 403.

Crotonaldehyde condensation; condensation with acid amides. H. L. DU MONT and G. RÄTZEL (Ber., 1939, 72, [B], 1500—1505).—The condensation of $\text{CHMe}:\text{CH}:\text{CHO}$ (I) with $\text{HCO}\cdot\text{NH}_2$ gives $\text{C}_5\text{H}_7\text{N}$ in very small amount probably because only the *cis*-form of (I) can act in this direction and it is present only in a very small proportion in technical (I). In the reaction between (I) and NH_2Ac the reactions of the *cis*- and *trans*-forms of (I) are concurrent. The attempted isomerisation to the *cis*-form by irradiation resulted in a general acceleration of the reaction. $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ which has preformed Me in the *cis*-position does not give the desired isoquinoline or 3-

methylisoquinoline with $\text{HCO}\cdot\text{NH}_2$ or NH_2Ac , probably because the activating effect of CHO is not so well transmitted through an aromatic nuclear double linking as through a simple vinyl group. Bu^tCHO and $\text{HCO}\cdot\text{NH}_2$ do not appear to afford $\text{C}_5\text{H}_7\text{N}$, dihydropyridine, or piperidine, and nitrogenous products are not derived from NH_2Ac . $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHO}$ and $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{CHO}$ tend to intramol. loss of HCl with formation of the unsaturated aldehyde rather than to elimination of HCl between the Cl of the aldehyde and H from NH_2Ac ; the latter functions essentially as acceptor for the acid and therefore forms diacetamide hydrochloride in both cases. Heterocyclic compounds are not obtained from $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NH}_2$ and EtCHO . H. W.

Catalytic preparation of acetone. A. TIAN and (MILLER) S. VIAN (Bull. Soc. chim., 1939, [v], 6, 1436—1447).—The yield of COMe_2 from AcOH passed over $\text{Ca}(\text{OAc})_2$ or $\text{Ba}(\text{OAc})_2$ on pumice is max. (81%) at ~620°. From 600° to 900°, CO_2 formed decreases and CO and CH_4 increase. $\text{Pb}(\text{OAc})_2$ is unsatisfactory as a catalyst, being reduced. E. W. W.

Mutarotation of xylose.—See A., 1939, I, 478.

Elucidation of the configuration at the glucosidic carbon atom in sugars by formation of ammonium salts. K. HESS and K. E. HEUMANN (Ber., 1939, 72, [B], 1495—1499).—Exceptions are noted to Mischeel's rule according to which only α -1-halogenoacetyl sugars react with NMe_3 with production of quaternary bases, which occurs with Walden inversion. It is uncertain whether halogeno-derivatives of furanose sugars and those of pyranose forms react essentially in opposite directions or whether Mischeel's rule cannot be generalised. 4-Chloro-2 : 3 : 6-trimethyl-*d*-glucofuranose 5-*p*-toluenesulphonate in C_6H_6 is converted by NMe_3 in abs. EtOH at -80° and then at room temp. into trimethyl-5-*p*-toluenesulphonyl-2 : 3 : 6-trimethyl- β -*d*-glucofuranosidoammonium chloride (I), m.p. 133°, $[\alpha]_D^{20}$ -48.9° in MeOH, -47.1° in H_2O , -45.7° in CHCl_3 (apparently unaccompanied by any dextrorotatory material), and 2 : 3 : 6-trimethyl-1-ethyl- α -*d*-glucofuranoside 5-*p*-toluenesulphonate (II), $[\alpha]_D^{20}$ +60.6° in MeOH, +59.8° in CHCl_3 , +57.7° in C_6H_6 . Na and 80% EtOH at room temp. transform (I) into trimethyl-2 : 3 : 6-trimethyl- β -*d*-glucofuranosidoammonium chloride, m.p. 165°, $[\alpha]_D^{20}$ +67.7° in H_2O , whereas when similarly treated (II) gives 2 : 3 : 6-trimethyl-1-ethyl- α -*d*-glucofuranoside, $[\alpha]_D^{20}$ +66.6° in CHCl_3 , +65.6° in C_6H_6 , +63.4° in MeOH. H. W.

Esters of methanesulphonic acid in the sugar group. B. HELFERICH, H. DRESSLER, and R. GRIEBEL (J. pr. Chem., 1939, [ii], 153, 285—299).—Gradual addition of MeSO_2Cl to anhyd. glucose in $\text{C}_5\text{H}_5\text{N}$ at -20°, keeping the mixture at 0°, and subsequent treatment with Ac_2O affords β -*d*-glucose tetra-acetate 6-methanesulphonate (I), m.p. 156°, $[\alpha]_D^{20}$ +10.1° in CHCl_3 , in ~29% yield. (I) is converted by anhyd. NaI in COMe_2 at 100° into β -*d*-glucose tetra-acetate 6-iodohydrin, m.p. 152—153°, $[\alpha]_D^{20}$ +9.1° in CHCl_3 . Analogously the by-product in the prep. of (I) gives α -*d*-glucose tetra-acetate 6-iodohydrin, m.p. 180—181° (corr.), $[\alpha]_D^{20}$ +101.0° in CHCl_3 . This is

transformed by Zn dust and 70% AcOH at 80–85° into α -D-isorhamnose tetra-acetate, m.p. 119.5° (corr.), $[\alpha]_D^{20} +123.8^\circ$ in CHCl_3 , which with $\text{HBr}\cdot\text{AcOH}$ at 0° gives acetobromo-D-isorhamnose, m.p. 143.5–144° (corr.), $[\alpha]_D^{18} +247^\circ$ in CHCl_3 . 1:2:5:6-Diisopropylidene-glucose is transformed by MeSO_2Cl in $\text{C}_5\text{H}_5\text{N}$ into 1:2:5:6-diisopropylidene-glucose 3-methanesulphonate (II), m.p. 83–84° (corr.), $[\alpha]_D^{19} -50.0^\circ$ in CHCl_3 , which with $\text{H}_2\text{SO}_4\cdot\text{aq. MeOH}$ affords D-glucose 3-methanesulphonate, m.p. 133–134° (corr.), $[\alpha]_D^{20} +77.0^\circ$ to $+56.9^\circ$ in H_2O during 2 days. This is converted by Ac_2O and NaOAc at 100° into β -D-glucose tetra-acetate 3-methanesulphonate, m.p. 169–170° (corr.), $[\alpha]_D^{19} +1.5^\circ$ in CHCl_3 , transformed by $\text{HBr}\cdot\text{AcOH}$ containing Ac_2O into α -D-bromoglucose 2:4:6-triacetate 3-methanesulphonate, (III) $[\alpha]_D^{19} +160^\circ$ in CHCl_3 . (II) is converted similarly into α -D-bromoglucose 2:6-diacetate 3-methanesulphonate (IV), m.p. 136–137° (corr.; decomp.), $[\alpha]_D^{19} +170^\circ$ in CHCl_3 . Ag_2CO_3 and MeOH transform (III) into methyl- β -D-glucoside triacetate 3-methanesulphonate, m.p. 128–128.5° (corr.), $[\alpha]_D^{19} -21.7^\circ$ in CHCl_3 , and (IV) into methyl- β -D-glucoside 2:6-diacetate 3-methanesulphonate, m.p. 105° (corr.), $[\alpha]_D^{19} -56.8^\circ$ in CHCl_3 . PhOH , KOH , and (IV) yield phenyl- β -D-glucoside 2:6-diacetate 3-methanesulphonate (V), m.p. 134.5–135° (corr.), $[\alpha]_D^{19} -56.6^\circ$ in CHCl_3 , which gives phenyl- β -D-glucoside 2:4:6-triacetate 3-methanesulphonate, m.p. 154–154.5°, $[\alpha]_D^{18} -27.0^\circ$ in CHCl_3 . Deacetylation of (V) by NaOMe in $\text{CHCl}_3\cdot\text{MeOH}$ affords phenyl- β -D-glucoside 3-methanesulphonate, m.p. 175° (corr.; decomp.), $[\alpha]_D^{19} -28.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$. (II) is hydrolysed by aq. AcOH to non-cryst. 1:2-isopropylidene-glucosylfuranose 3-methanesulphonate, $[\alpha]_D^{18} -20.6^\circ$ in H_2O , converted by $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ into 1:2-isopropylidene-glucosylfuranose 5:6-diacetate 5-methanesulphonate, m.p. 136–136.5° (corr.), $[\alpha]_D^{19} -2.3^\circ$ in CHCl_3 . This is transformed by $\text{HBr}\cdot\text{AcOH}$ containing Ac_2O into α -D-bromoglucose 2:5:6-triacetate 3-methanesulphonate, m.p. 123–123.5° (corr.), $[\alpha]_D^{19} +191.5^\circ$ in CHCl_3 . Diisopropylidene-galactose and MeSO_2Cl in $\text{C}_5\text{H}_5\text{N}$ at 0° yield 1:2:3:4-diisopropylidene-galactopyranose 6-methanesulphonate, m.p. 122°, $[\alpha]_D^{20} -62.0^\circ$ in CHCl_3 . H. W.

Acyl migration in a derivative of galactose. J. S. D. BACON, D. J. BELL, and H. W. KOSTERLITZ (J.C.S., 1939, 1245–1250).—4:6-Benzylidene- β -methylgalactoside (improved prep.) is converted by $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{C}_6\text{H}_6$ at 38° for 24 hr. into 4:6-benzylidene- β -methylgalactoside 2:3-dibenzoate (I), m.p. 195–196°, $[\alpha]_D^{17} +156.1^\circ$ (all in CHCl_3 unless stated otherwise), which with boiling $\text{COMe}_2\cdot 0.25\text{N}\cdot\text{HCl}$ gives β -methylgalactoside 2:3-dibenzoate (II), m.p. 136.5–138.5°, $[\alpha]_D^{19} +101.9^\circ$, or (+1 CHCl_3), m.p. 80°, $[\alpha]_D^{19} +80.6^\circ$ [$\text{PhCHO}\cdot\text{ZnCl}_2$ gives (I), m.p. 198°]. (I) and $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{C}_6\text{H}_6$ afford β -methylgalactoside 2:3:6-tribenzoate (III), m.p. 143–144°, $[\alpha]_D^{18} +56.1^\circ$ [its 4-p-toluenesulphonate (IV), m.p. 175°, $[\alpha]_D^{20} +58.9^\circ$, is unaffected by $\text{NaI}\cdot\text{COMe}_2$ at 100°]. Methylation (Purdie's reagents) (method: Levene *et al.*, A., 1932, 1115) of (III) gives a dimethylhexose tribenzoate, debenzoylated (Zemplén) to an amorphous product (OMe 27%) and 2-methyl- β -methylgalactoside, m.p. 132–133°, $[\alpha]_D^{18} +1.2^\circ$ (cf. Oldham *et al.*, A., 1938, II,

127). This acyl migration in the galactose series is discussed. *iso*Propylidene- β -methylgalactoside and $\text{CPh}_3\text{Cl}\cdot\text{C}_5\text{H}_5\text{N}$ (method: Bell *et al.*, 1938, II, 393) give a product, converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}\cdot\text{C}_5\text{H}_5\text{N}$ at 38° for 48 hr. into 6-triphenylmethyl-3:4-*iso*-propylidene- β -methylgalactoside 2-p-toluenesulphonate, m.p. 163–164°, $[\alpha]_D^{21} -8.4^\circ$. Change in α with a solution of (IV) in $\text{COMe}_2\cdot\text{H}_2\text{O}\cdot\text{N}\cdot\text{HCl}$ at 100° is very small; the resulting (after 220 min.) β -methylgalactoside 2-p-toluenesulphonate has m.p. 143–144°, $[\alpha]_D^{21} -23.7^\circ$ in EtOH (3:4:6-tribenzoate, m.p. 143–144°, $[\alpha]_D^{18} +45.5^\circ$). A. T. P.

Syntheses of glycosides. XI. Cichoriin. F. S. H. HEAD and A. ROBERTSON (J.C.S., 1939, 1266–1267; cf. A., 1931, 73).—Esculetin and $\text{BzCl}\cdot\text{aq. NaOH}$ give 6-O-benzoyl-esculetin (I), m.p. 198° (sinters at 185°), and the 6:7-O-dibenzoate, m.p. 186°. (I) and $\text{MeI}\cdot\text{K}_2\text{CO}_3\cdot\text{COMe}_2$ give 6-benzoyloxy-7-methoxycoumarin, m.p. 217–218° (*loc. cit.*), converted by $\text{NH}_3\cdot\text{MeOH}$ at 0°, then aq. HCl , into 7-O-methyl-esculetin. (I), O-tetra-acetyl- α -glucosidyl bromide, and active Ag_2O give 7-O-tetra-acetyl- β -glucosidoxy-6-benzoyloxy-coumarin, m.p. 218°, which with $\text{NH}_3\cdot\text{MeOH}$ at 0° gives 6-hydroxy-7- β -glucosidoxycoumarin (cichoriin), m.p. 213–214°, $[\alpha]_D^{20} -104^\circ$ in aq. dioxan (Ac_5 derivative, m.p. 218°), identical with a natural specimen. A. T. P.

Chemical examination of the fruit of *Pittosporum undulatum*. J. W. CORNFORTH and J. C. EARL (J. Proc. Roy. Soc. New South Wales, 1939, 72, 249–254).—Extraction of the dried fruit with Et_2O gives a small amount of unidentified material, m.p. 51–52°, and pentatriacontane, m.p. 73–75°. The alcoholic extract of the fruit gives a non-separable mixture of a saponin and an anthocyanidin. Addition of CaCl_2 to a solution of the evaporated extract in H_2O gives a ppt. rich in leucoanthocyanin which is hydrolysed by $\text{HCl}\cdot\text{H}_2\text{O}\cdot\text{EtOH}$ to cyanidin. Hydrolysis of the alcoholic extract affords a mixture from which CHCl_3 removes *pittosapogenin*, $\text{C}_{30}\text{H}_{50}\text{O}_7$, m.p. 308–310°, $[\alpha]_D^{20} 27.8^\circ$ in $\text{CHCl}_3\cdot\text{MeOH}$ (acetate, m.p. 252–254°). Glucose (I), galactose (II), and a little mannose are formed during the hydrolysis; pentoses, glycuronic acid, and ketoses are absent. The separation of (I) and (II) by $\text{NPhMe}\cdot\text{NH}_2$ is greatly improved by allowing the galactosephenylmethylhydrazone to crystallise for two days in the ice-chest instead of for 6 hr. at room temp. H. W.

Gentiopicroin. II. Y. ASAHINA and Y. SAKURAI (Ber., 1939, 72, [B], 1534–1540; cf. A., 1936, 731).—The maximal formation of eugentiogenin (I) accompanied by an almost equal amount of Tanret's gentiogenin (II) is observed when the enzymic hydrolyses of gentiopicroin (III) takes place at 35–37° and $p_{\text{H}} 3.4$. At $p_{\text{H}} 7.2$ the production of (II) reaches its max. at the expense of (I), so that primarily formed (I) appears to pass in the presence of emulsin into (II). Continuous extraction with Et_2O of a solution containing (III) and emulsin gives optically inactive mesogentiogenin (IV) as a viscous, yellow oil which polymerises within a few days to an amorphous mass. It gives a blue colour with FeCl_3 . It is $\text{C}_{10}\text{H}_{10}\text{O}_4$ since it passes into tetrahydromesogentiogenin (V), $\text{C}_{10}\text{H}_{14}\text{O}_4$, m.p. 103°. In H_2O in presence of emulsin (IV)

passes into (I) and (II). Takadiastase converts (IV) into (II). Hence (IV) is probably the primary product of the hydrolysis of (III). In respect of its optical inactivity and formation of (V) there is a difference between (IV) and the hypothetical protogentiogenin attributed to spontaneous at. displacements at the moment of elimination of the sugar. Gentiopicrotin tetra-acetate (VI) is hydrogenated in EtOH or EtOAc to α - (VII), m.p. 208° $[\alpha]_D^{25} -48.06^{\circ}$ in CHCl_3 , and (possibly non-homogeneous) β - (VIII), m.p. 159° , $[\alpha]_D^{25} -98.80^{\circ}$ in CHCl_3 , *tetrahydrogentiopicrotin tetra-acetate*. Chlorination of a mixture of (VII) and (VIII) in CHCl_3 and crystallisation of the product leads to the isolation of *tetrahydrogentiopicrotin tetra-acetate dichloride*, m.p. 161° , which is stable towards KMnO_4 in COMe_2 ; it is obtained almost quantitatively from (VII) whereas (VIII) affords essentially a non-cryst. product. Hydrogenation (Pd-C in AcOH) of (VI) gives *hexahydrogentiopicrotin tetra-acetate* (IX), m.p. 154° , $[\alpha]_D^{25} -54.24^{\circ}$ in CHCl_3 , also obtained directly from (VII); under similar conditions (VIII) gives a non-homogeneous product from which (IX) can be isolated. The previous observation that (III) loses 1 mol. of AcOH when acted on by KOH-EtOH could not be confirmed. After removal of sugar the freshly prepared (IV) is heated under pressure with Ba(OH)_2 , which causes the loss of 1 mol. each of CO_2 and HCO_2H . Since (III) does not give an additive product with maleic anhydride it does not appear to contain a conjugated double linking. (II) is unchanged when heated in EtOH at 220° or in boiling xylene. The salt obtained by the hydrolysis of (III) is unaffected by prolonged contact with cold alkali and (III) is regenerated by the addition of acid. H. W.

Kikyo root. VII. Mol. wt. and hydrolysis of platycodin. M. TSUJIMOTO and T. MATSUMOTO (J. Agric. Chem. Soc. Japan, 1939, 15, 690—695).—Platycodin, $\text{C}_{42}\text{H}_{68}\text{O}_{17}$, is completely hydrolysed to *platycodigenin*, $\text{C}_{30}\text{H}_{48}\text{O}_7$, and glucose in 20 hr. by boiling 5% EtOH-HCl or in 100 hr. by boiling 5% EtOH- H_2SO_4 . J. N. A.

Composition and properties of soluble starch. C. DUMAZERT and G. SANTONI (Compt. rend., 1939, 209, 127—129).—A solution of starch from wheat, arrowroot, maize, potato, and rice after treatment with cold NaOH has $[\alpha]_D +189^{\circ}$ and does not gel when cooled. It gives a Ac_2 derivative and is oxidised by I in an alkaline medium, from the extent of which, before and after hydrolysis, the min. mol. wt. is calc. to be 3258. J. L. D.

"Faults" in cellulose molecules. H. STAUDINGER and A. W. SOHN (Naturwiss., 1939, 27, 548—549).—Two forms of cellulose (I) chain are distinguished: (i) the normal, containing an uninterrupted series of pyranoid glucose units and represented by repptd. (I), in which the degree of polymerisation in Schweizer's reagent equals that of the nitrate (II); (ii) a second form containing reactive "faults" of an ester nature which suffer fission with alkali but not with conc. HNO_3 ; this can be formed from normal (I) by oxidation of a glucose unit to a product containing CO_2H . Oxycellulose in Schweizer's reagent has therefore a much smaller degree of poly-

merisation than (II), due to degradation by the reagent. Treatment of (II) with dil. alkali, however, lowers the degree of polymerisation to that of the former. The technical implications of this are discussed.

S. H. H.

System cellulose-sodium hydroxide-water.—See A., 1939, I, 512.

Condensation products of aldehydes with amines.—See A., 1939, I, 510.

Microscopy of the amino-acids and their compounds. IV. Picrolonates. R. DUNN, K. INOUE, and P. L. KIRK (Mikrochem., 1939, 154—160; cf. A., 1937, II, 314).—Characteristic crystal habits and optical data are described for the salts of picrolonic acid with 27 NH_2 -acids. The predominant crystal habit is acicular, the needles being usually arranged in rosettes. In nearly all cases the n of the crystals can serve for identification. J. W. S.

Nickel salts of amino-acids: their solubility. K. LANG (Biochem. Z., 1939, 301, 368—370).—The salts (2 mols. acid residue to 1 Ni) are prepared by boiling aq. solutions of the acids with NiCO_3 until evolution of CO_2 ceases. The $l(+)$ -valine salt is anhyd. but the salts of glycine, *dl*-alanine, *dl*-amino-butyric acid, *l*-leucine, *dl*-isoleucine, and *l*-proline contain $2\text{H}_2\text{O}$. The solubilities of the salts in H_2O and MeOH are recorded. Although considerable differences in solubility exist, the separation of NH_2 -acids (e.g., from protein hydrolysates) by means of the salts is not practicable. W. McC.

Cosubstrates in proteolysis. O. K. BEHRENS and M. BERGMANN (J. Biol. Chem., 1939, 129, 587—602; cf. A., 1939, II, 463).—*Carbobenzyl-oxy-l*, m.p. 122 — 123° , and *d-leucineamide*, m.p. 123 — 124° , are hydrogenated (Pd-black; AcOH-MeOH) to *l*- (I), m.p. 125 — 126° , $[\alpha]_D^{25} +9.25^{\circ}$ in H_2O , and *d-leucineamide acetate*, m.p. 125 — 127° , $[\alpha]_D^{25} -9.3^{\circ}$ in H_2O , respectively. (I) and *l-leucineanilide* (II) are hydrolysed slowly by cysteine-activated papain (A) (citrate buffer, p_H 5.0); e.g., (I) shows a 75% fission (optimum at p_H 5) at 40° in 5 days, and (II), 57% in 6 days. *d-Leucineamide* shows no fission after 4 days at 40° . The action of various papain preps. on (I) and carbobenzyl-oxy-*l-isoglutamine* is compared. Carbobenzyl-oxy-*l*-glutamic acid, N-NaOH , NH_2Ph , and (A) at 40° give the anilide, m.p. 193 — 195° , $[\alpha]_D^{25} -15.3^{\circ}$ in 95% EtOH, hydrogenated to glutam-monoanilide (III), m.p. 193 — 194° . Glycine-amide (IV) or -anilide (V), or (III), is resistant to (A); the anilides are, however, hydrolysed slowly (17 and 41% fission in 4 days, respectively) in presence of horse serum (has no effect alone), which thus produces substances enabling (A) to effect hydrolysis. (IV) (35% in 6 days) or (V) or (III) is hydrolysed by (A) when acetyl-*dl*-phenylalanylglycine (VI) (cosubstrate) is present; thus (V) gives acetyl-*l*-phenylalanylglycineanilide (VII), m.p. 207 — 208° , acetylphenylalanylglycylglycineanilide, m.p. 242 — 243° , (VI), NH_2Ph , and glycine. (V) and acetyl-*l*-phenylalanylglycine probably first give acetyl-*l*-phenylalanylglycylglycineanilide, hydrolysed to glycine and NH_2Ph , some of the latter then forming acetyl-*l*-phenylalanylglycineanilide. Acetyl-*dl*-phenylalanine (V), and (A) show no reaction. (V)

(as acetate) and carbobenzyloxy-*l*- (VIII) or -*d*-phenylalanylglycine in presence of (A) (7 days) gives a nearly quant. yield of carbobenzyloxy-*l*-, m.p. 213°, $[\alpha]_D^{25}$ -3.3° in AcOH, or -*d*-phenylalanylglycylglycineanilide, m.p. 213—214°, $[\alpha]_D^{25}$ +3.1° in AcOH, respectively (not attacked by enzyme solution). (V) and benzoyl-*dl*-phenylalanylglycine similarly give (1 + *dl*)-benzoyl-phenylalanylglycylglycineanilide, m.p. 236—240°. (VIII), (III), and (A) give carbobenzyloxy-*l*-phenylalanylglycyl-*l*-glutam-monoanilide, m.p. 213—215°. Carbo-benzyloxyglycine and (III) + (A) give carbobenzyloxy-glycyl-*l*-glutamanilide, m.p. 182°. Glycyl-*l*-leucine is not hydrolysed by (A), but catalysis by (VI) gives, through acetylphenylalanyldiglycyl-leucine, free glycine and *l*-leucine; 88% of (VI) is recovered and there is 65% hydrolysis in 29 hr., almost complete in a few days; the mechanism is discussed. (V) is slowly split by (A) when proteins, e.g., blood fibrin, gelatin, casein, are present, and these, on hydrolysis, give products which act as "cosubstrates." Carbo-benzyloxytyrosineamide is hydrogenated to *l*-tyrosineamide acetate (IX), m.p. 177°, which with (VIII) and (A) give carbobenzyloxy-*l*-phenylalanylglycyl-*l*-tyrosineamide, m.p. 248° (decomp.) (darkens at 243°). (IX), (VI), and (A) give free tyrosine (80% hydrolysis). Glycine anhydride and acetamidocinnamic acid azlactone, in aq. NaOH-COMe₂, give acetyldehydrophenylalanylglycylglycine, m.p. 223—224°, hydrogenated (Pd-black; AcOH-MeOH) to acetyl-*dl*-phenylalanylglycylglycine (XI), m.p. 183—184° [57% hydrolysis by (A) in 3 days] [amide (XII), m.p. 203—206°, from (XIII)]. (XI) and CH₂N₂-MeOH-Et₂O give the *Me* ester (XIII), m.p. 158—159°, converted by N₂H₄·H₂O-EtOH into acetyl-*dl*-phenylalanylglycylglycine hydrazide, m.p. 200—202°, which through the azide affords the anilide, m.p. 229—231°. This is hydrolysed slowly by (A) (16% of each of the peptide bonds in 3 days), but (XII) is hydrolysed more readily to acetylphenylalanylglycine, glycine, and NH₃. (XI), NH₂Ph, and (A) give (VII).

A. T. P.

Physico-chemical analysis of reactions of organic amides with acids. Carbamide with fatty acids.—See A., 1939, I, 524.

Preparation of cyanogen iodide.—See A., 1939, I, 483.

Amidines and amidoximes with trypanocidal activity. I. D. LAMB and A. C. WHITE (J.C.S., 1939, 1253—1257; cf. King *et al.*, A., 1938, III, 63).—Alkylenedicarbonamidoximes, [CH₂]_n[C(NH₂)₂:N-OH]₂, are prepared (readily when *n* = 5 or 10—13; with difficulty when *n* = 7—9) from [CH₂]_nCN₂ (A) and NH₂OH by Tiemann's method (A., 1884, 734). The following are described: *pentane-αα**, m.p. 142—144° (dihydrochloride, m.p. 150—155°), *heptane-αα**, m.p. 156°, *nonane-αα**, m.p. 167°, *decane-αα*-†, m.p. 184—186° (decomp.) (dihydrochloride, m.p. 149—158°; Ac₂ derivative, m.p. 129°), *undecane-αα*-† (I), m.p. 166° (dihydrochloride, m.p. 178°), and *tridecane-αα*-dicarbonamidoxime † (II), m.p. 170° (dihydrochloride, m.p. 158—160°). *Diphenyl*-, m.p. 245° (decomp.) (dihydrochloride, m.p. 290° (decomp.)), *diphenylmethane*-, m.p. 215° (previous sintering) (dihydrochloride, decomp. 220°), *dibenzyl*-, decomp. ~243° (dihydrochloride), and *stilbene-4 : 4'*-dicarbonamidoxime,

FF* (A, II.)

m.p. >320° (decomp.) (dihydrochloride, chars ~300°), are similarly prepared. *α*-Carbamyl*, m.p. 157—158° (hydrochloride, m.p. 144°), and *α*-cyano-undecane-λ-carbonamidoxime*, m.p. 87—88° (hydrochloride, m.p. 84°), accompany (I) and *α*-cyanotridecane-ν-carbonamidoxime*, m.p. 98° (hydrochloride, m.p. 96°), is formed with (II). *κ*-Cyanoundecoamide, m.p. 87°, *λ*-cyanododecoamide, m.p. 101°, and *ν*-cyanotetradecoamide, m.p. 103—104°, are formed as by-products during prep. of (A) from [CH₂]_nBr₂ and KCN. 4 : 4'-Dicyanostilbene, m.p. ~278° (after sintering), is obtained from the (NH₂)₂-[prep. from less fusible (NO₂)₂]-derivative. The following are prepared by the method of Easson *et al.* (A., 1932, 55): *decane-αδ*-dicarbonamidine dihydrochloride, m.p. 227—228° (decomp.), and picrate, m.p. 233°; *decanebis*-(NN'-*di*-phenyl)*, m.p. 163—165°, and (-N-cyclohexyl-carbonamidine*), m.p. 122° (dihydrochloride, m.p. 273°); *undecane-αλ*-dicarbonamidine (III) (dihydrochloride, m.p. 150—151°); *tridecane-αν*-dicarbonamidine (dihydrochloride, m.p. 165—167°; picrate, m.p. 190—191°), accompanied by the *αν*-dicarboxylamide, m.p. 176°; *α*-carbamyltridecane-ν-carbonamidine hydrochloride*, m.p. 164—165°; *tetradecanemonocarbonamidine* [hydrochloride*, m.p. 138° (after sintering); picrate, m.p. 166°]. *ακ*-Di-(4 : 5-dihydro-2-glyoxal-*inyl*)decane, m.p. 181° (hydrochloride, m.p. 183°; picrate, m.p. 223—224°), is obtained from decane-dicarboniminoethyl ether hydrochloride and EtOH-(CH₂-NH₂)₂ at 70°.

Compounds marked † have considerable activity against experimental mouse trypanosomiasis (*T. equiperdum*) but are less active than (III). Some of the compounds described possess slight activity, but those marked * are inactive.

H. B.

Thermal decomposition of azomethane.—See A., 1939, I, 476.

Mechanism of the attack of trimethylarsine and some quaternary arsonium salts by sulphuric acid. G. PETIT (Compt. rend., 1939, 209, 111—113; cf. A., 1937, II, 449).—The action of H₂SO₄ (*d* 1.83) on AsMe₃ at <250° yields AsMe₃O, which undergoes further degradation to As(OH)₃, without formation of intermediate compounds, at >280°. (AsMe₄)₂SO₄ is converted directly to As(OH)₃ in 6 hr. at 320°. [AsMe₃(C₂H₄-OH)]₂SO₄ reacts similarly (45 min. at 320°), the reaction occurring by scission and destruction of the C₂H₄-OH group followed by oxidation and degradation of the resulting AsMe₃. A similar process occurs with [AsMe₃(CH₂-CO₂H)]₂SO₄. The org. groups are eliminated with formation of CO₂, SO₂, and H₂O in each case.

A. J. E. W.

Complex nickel salts with quadri- and sexavalent central atom. H. GLASER and P. PFEIFFER [with W. RÜHLMANN] (J. pr. Chem., 1939, [ii], 153, 300—312).—The Ni compounds richest in amine from (CH₂-NH₂)₂ (= en) and NHEt·[CH₂]₂-NH₂ (X) have the composition [Ni en₂](ClO₄)₂·0.5H₂O and [NiX₃](ClO₄)₂, which in colour and constitution agree with the other Ni hexamine salts. The salts [Ni en₂(OH)₂](ClO₄)₂ and [Ni{CH₂-NHet}₂](OH)₂(ClO₄)₂ (II) are diaquo-compounds since their violet-blue colour changes to

orange when they are dehydrated. These latter salts contain Ni^{IV} . The orange salts immediately absorb H_2O from the air. (I) dissolves unchanged in MeOH whereas in hot MeOH (II) becomes dehydrated. The tendency to form salts with Ni^{IV} attains its max. in the salt, $[\text{Ni}(\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NET}_2)_2](\text{ClO}_4)_2$, which does not yield an aquo-salt. This is converted by KCNS in MeOH into the violet-blue salt, $[\text{Ni}(\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NET}_2)_2(\text{CNS})_2]$, which loses 1 mol. of base when heated and passes into the green compound, $[\text{Ni}(\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NET}_2)(\text{CNS})_2]$. H. W.

Ammonio-mannito-dimolybdc complexes.—See A., 1939, I, 484.

Dimerisation reactions of unsaturated hydrocarbons. E. BERGMANN (Trans. Faraday Soc., 1939, 35, 1025—1034).—Dimerisation of olefines gives cyclobutane derivatives by irradiation only; under the influence of catalysts it proceeds by migration of a H atom. Experimental evidence in support of these conclusions is reviewed. F. L. U.

Homogeneous thermal decomposition of cyclic hydrocarbons. L. KÜCHLER (Trans. Faraday Soc., 1939, 35, 874—880).—Thermal decomp. of cyclohexene at $758\text{--}838^\circ\text{K}/<200\text{ mm.}$ yields 80—90% of C_2H_4 + butadiene (I) and a negligible amount of C_6H_6 ; addition of H_2 (equal amount) or NO neither inhibits nor catalyses the reaction to any extent, indicating absence of radical chain mechanism. cycloHexane (II) decomposes more slowly, but contrary to Pease and Morton (A., 1933, 1017) does not give methylcyclopentane (III). The chief products are H_2 , C_2H_4 , C_3H_6 , and (I), indicating two mechanisms, $\text{C}_6\text{H}_{12} \rightarrow 2\text{C}_3\text{H}_6$, and $\rightarrow \text{H}_2 + \text{C}_6\text{H}_{10} \rightarrow \text{H}_2 + \text{C}_2\text{H}_4 + \text{(I)}$. NO has no influence on the velocity of decomp. and no explanation can be given for the period of negligible pressure change at the start of the reaction. The results for (III) were similar to those for (II), although the initial lag was less marked. F. R. G.

Preparation of [sodium] cyclopentylalkanesulphonates. S. PILAT and N. TURKIEWICZ (Ber., 1939, 72, [B], 1527—1531).—Aq. solutions of $\text{C}_5\text{H}_9\cdot[\text{CH}_2]_n\cdot\text{SO}_3\text{Na}$ have a larger surface activity when n is small and are more active than alkylated cyclohexane derivatives. β -cyclopentylethanol (modified prep. from cyclopentyl chloride) is converted into β -cyclopentylethyl chloride and thence by cryst. Na_2SO_3 at 200° into *Na* β -cyclopentylethanesulphonate. δ -cyclopentylbutanol, obtained in 5% yield from Mg cyclopentylmethyl chloride and $[\text{CH}_2]_3\text{O}$ or in 68% yield from Mg β -cyclopentylethyl bromide and $[\text{CH}_2]_2\text{O}$, is transformed by HBr and conc. H_2SO_4 into δ -cyclopentylbutyl bromide (I) and thence into *Na* δ -cyclopentylbutanesulphonate. The Grignard compound of (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\cdot[\text{CH}_2]_3\cdot\text{Cl}$ yield η -cyclopentylheptyl chloride, whence *Na* η -cyclopentylheptanesulphonate. Menthol is converted successively into menthyl bromide, β -menthylethanol, b.p. $132\text{--}136^\circ/10\text{ mm.}$, β -menthylethyl chloride, b.p. $120\text{--}125^\circ/10\text{ mm.}$, and *Na* β -menthylethanesulphonate. *Et* fencholate is reduced to the corresponding alcohol, which is converted into the chloride (II) and thence into *Na* dihydrofenchylsulphonate. (II) by successive condensation with $\text{CHNa}(\text{CO}_2\text{Et})_2$, hydrolysis, and decarboxylation yields dihydrofenchylacetic acid, b.p.

$165\text{--}166^\circ/10\text{ mm.}$, the *Et* ester, b.p. $146\text{--}148^\circ/10\text{ mm.}$, of which is reduced to β -dihydrofenchylethanol, b.p. $134\text{--}135^\circ/10\text{ mm.}$, whence β -dihydrofencholethyl chloride, b.p. $120\text{--}126^\circ/10\text{ mm.}$, and *Na* dihydrofenchylethanesulphonate. H. W.

***n*-Octylcyclohexane**, b.p. $117\text{--}119^\circ/11\text{ mm.}$ —See A., 1939, I, 516.

Catalytic ring-closure of open-chain hydrocarbons.—See A., 1939, I, 530.

Cyclisation (aromatisation) of aliphatic hydrocarbons. H. HOOG, J. VERHEUS, and F. J. ZUIDERWEG (Trans. Faraday Soc., 1939, 35, 993—1006).—Quant. analysis of the products obtained by passing a large no. of hydrocarbons over Cr_2O_3 at 465° and 1 atm. (contact time 20 sec.) shows that aromatisation occurs to a marked extent only with those hydrocarbons with structure permitting direct formation of a 6-C ring. *sec.* C atoms preferentially take part in ring closure. Cyclisation of paraffins and olefines containing ≤ 8 C also involves cracking, which increases with the no. of C atoms. The degree of aromatisation increases in the order paraffins < olefines < 6-ring naphthenes < 6-ring cycloolefines. Cr_2O_3 promotes shift of the double bond in an olefine to a more central position. A general conclusion is that cyclisation of a paraffin proceeds largely through dehydrogenation to the corresponding olefine. F. L. U.

Ozonisation of allyl-, propenyl-, and α -methylvinyl-benzene.—See A., 1939, I, 401.

Aryl iodochlorides. I. R. NEU (Ber., 1939, 72, [B], 1505—1512).— ArICl_2 most closely resemble metallic halides; the *ArI* portion is very similar to a metal in a higher state of oxidation from which it readily passes into a lower state. $\text{PhI}(\text{OAc})_2$ is best obtained by the interaction of PhICl_2 and $\text{Pb}(\text{OAc})_2$ in AcOH containing 10% of Ac_2O . PhICl_2 and $\text{Pb}(\text{CNS})_2$ in CHCl_3 , CCl_4 , or CH_2Cl_2 give a solution of CNS , which converts NH_2Ph into *p*-thiocyananiline, m.p. $56\text{--}57^\circ$, PhOH into *p*-thiocyanophenol, m.p. $59\text{--}60^\circ$, NPhMe_2 into *p*-thiocyanodimethylaniline, m.p. $73\text{--}74^\circ$, *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ into 2-amino-5-thiocyanophenol, m.p. 98° , and *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ into 3-amino-6-thiocyanophenol, m.p. $107\text{--}109^\circ$. Similar treatment of *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ gives black, non-homogeneous products. *o*- $\text{C}_6\text{H}_4(\text{OH})_2$ in EtOAc and CNS in CH_2Cl_2 afford 1:2:4- $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CNS}$, m.p. 142° . Dithiocyanobenzidine decomposes at $>365^\circ$ (lit. 250°). *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ does not appear to be attacked by CNS , prolonged contact giving $(\text{CNS})_n$; the use of Fe as catalyst in Et_2O , EtOAc , or AcOH brings no advantage. *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ and CNS in CHCl_3 at room temp. afford 1-amino-5-ethoxybenzthiazole, m.p. 164° , whilst thymol and CNS in CCl_4 yield 6-thiocyano-4-isopropyl-*m*-cresol, m.p. $108\text{--}109^\circ$. *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ gives 5-thiocyananthranilic acid, m.p. $173\text{--}174^\circ$. 1-Thiocyano-2-naphthol, m.p. 113° , and 1-thiocyano-2-naphthylamine or 1-aminonaphthothiazole, m.p. 260° , are derived from $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, respectively. PhICl_2 and PhOH , NHPhAc , *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ in suitable media give, respectively, *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, (after hydrolysis) *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, 2:5:1- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{H}$, and 1:2- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{OH}$. $\text{PhI}(\text{OAc})_2$ converts NH_2Ph

in C_6H_6 at room temp. into azobenzene; an ill-defined product, possibly 3:7-diethoxyphenazine, is derived from $PhI(OAc)_2$ and $p-NH_2 \cdot C_6H_4 \cdot OEt$ in $AcOH$.

H. W.

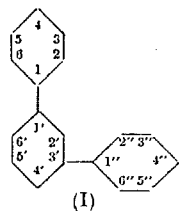
Isomerisation of carotenes. III. Change of β -carotene into ψ - α -carotene. G. P. CARTER and A. E. GILLAM (Biochem. J., 1939, 33, 1325—1331; cf. A., 1937, II, 405; Zechmeister *et al.*, A., 1938, II, 400).—The conversion of β - (I) into ψ - α - (II) -carotene is spontaneous and not due to adsorption on Al_2O_3 or $Ca(OH)_2$. The final product is an equilibrium mixture containing ~31% of (II). The rate of transformation in C_6H_6 -light petroleum is slow at -2° (2.5% isomerisation in 12 weeks) and $\sim 20^\circ$ (11% in 7 weeks) but equilibrium is attained in 3 hr. at 80° . The reverse change is more rapid (5—6% in 8 weeks at -2° , 31% in ~0.5 hr. at 80°). (I) is separated from (II) by crystallisation (after boiling) or adsorption on Al_2O_3 or $Ca(OH)_2$. If absorption spectra are used for control, α -carotene and (II) can be chromatographically differentiated and separated.

W. McC.

Reversible isomerisation of carotenoids by iodine catalysis. L. ZECHMEISTER and P. TUZSON (Ber., 1939, 72, [B], 1340—1346; cf. A., 1938, II, 400).—Under the influence of I or heat the following reversible isomerisations are recorded: lycopene \rightleftharpoons neolycopene; β - to ψ - α -carotene; kryptoxanthin to neokryptoxanthin; lutein (xanthophyll) to neolutein-A and -B; zeaxanthin to neozeaxanthin-A, -B, and -C; taraxanthin to neotaraxanthin-A, -B, and -C. The absorption of the products lies in a region of shorter λ than that of the initial materials. In the case of the hydrocarbons and kryptoxanthin the newly formed zones lie close beneath those of the unchanged pigment. If, however, at least two OH are present in the mol., the isomerised fraction has a greatly enhanced adsorption affinity and remains in the topmost zone, whereas, on development, the initial material passes much lower, whilst the new colour zone consists of two or three components which remain close to one another. The processes of isomerisation are in all cases reversible. The phenomena cannot at present be explained and the nomenclature is therefore provisional. Probably *cis-trans* displacements play a decisive part and, possibly, differences in configuration of $>CH \cdot OH$ in the polyene alcohols.

H. W.

Terphenyl series. III. Preparation and nitration of *m*-terphenyl [*m*-diphenylbenzene]. H. FRANCE, I. M. HEILBRON, and D. H. HEY (J.C.S., 1939, 1288—1292).—5-Chloro-3-phenyl- Δ^5 -cyclohexenone is reduced (H_2 , colloidal Pd, EtOH, room temp.) to 3-phenylcyclohexanone, converted by $MgPhBr$ into a carbinol, which is dehydrated (98% HCO_2H) to 1:3-diphenyl- Δ^3 - and/or - Δ^2 -cyclohexene, b.p. 198—200°/18 mm. This is dehydrogenated (S in boiling quinoline) to *m*-terphenyl (I), m.p. 89° . $m-C_6H_4Ph \cdot NO_2$ (63% yield from $m-NO_2 \cdot C_6H_4 \cdot NAc \cdot NO$ and C_6H_6) is converted (usual methods) into $m-C_6H_4Ph \cdot NAc \cdot NO$, which with C_6H_6 gives (I). Nitration of (I) is reinvestigated (cf. Wardner *et al.*, A., 1932, 940). HNO_3 (d 1.42) - $AcOH$ at 85 — 90° affords 4'-nitro-*m*-terphenyl [4-nitro-1:3-diphenylbenz-



ene] (II), distils at $80^\circ/10^{-2}$ mm. (whence 4'-amino- and 4'-acetamido-*m*-terphenyl, m.p. 116—117°); HNO_3 (d 1.42) at 80 — 90° gives the ? 4:4' or 4':4''-(NO_2)₂-derivative, m.p. 213—215° [oxidised (CrO_3 , $AcOH$) to $p-NO_2 \cdot C_6H_4 \cdot CO_2H$], whilst HNO_3 (d 1.5) - $AcOH$ at 40 — 100° yields (probably) the 4:4':4''-(NO_2)₃-derivative, m.p. 199—200° [also from (II) and HNO_3 (d 1.5) - $AcOH$ at 30 — 90°]. Oxidation (CrO_3 , $AcOH$) of (II) gives 2-nitrodiphenyl-5-carboxylic acid, m.p. 220—221°, similarly obtained from 2-nitro-5-methyldiphenyl, m.p. 86—87° (from 2:4:1- $NO_2 \cdot C_6H_3Me \cdot NAc \cdot NO$ and C_6H_6 at 35°).

H. B.

Absorption spectra and structure of compounds containing chains of benzene nuclei.—See A., 1939, I, 449.

Hydrogenation of naphthylamines.—See B., 1939, 917.

Formation of aryltrimethylammonium iodides in methyl-alcoholic solution.—See A., 1939, I, 527.

Kinetics of the formation of *o*-substituted phenyltrimethylammonium iodides in methyl-alcoholic solution.—See A., 1939, I, 527.

Optical inversion of the benzyl derivatives of *d*-cysteine and *d*-homocysteine *in vivo*.—See A., 1939, III, 936.

Benzylisothiocarbamide and its application to the identification of organic acids. S. VEIBEL and K. OTTUNG (Bull. Soc. chim., 1939, [v], 6, 1434—1435).—By the method previously described (A., 1938, II, 390; cf. also Donleavy, A., 1936, 1005), the following benzylisothiocarbamide salts are obtained: dl-malate, m.p. 159—160°; mucate, m.p. 194—195°; mono-, m.p. 159—160°, di-, m.p. 178—179°, and tri-chloroacetate, m.p. 148—149°; α -bromopropionate, m.p. 158—159°; azelate, m.p. 163—164°; *o*-toluate, new m.p. 145—146°; *p*-hydroxybenzoate, m.p. 143—145°; α -, m.p. 158—159°, and β -hydroxynaphthoate, m.p. 216—217°; phthalate, new m.p. 157—158°; *H* isophthalate, m.p. 215—216°; terephthalate, m.p. 202—206°; pyromucate, m.p. 211—212°.

E. W. W.

Sulphanilhydroxylamide.—See B., 1939, 995.

***cis*-Azo-compounds. II.** A. H. COOK and D. G. JONES (J.C.S., 1939, 1309—1315).—The following are obtained by the procedure previously described (A., 1938, II, 317): *cis*-*m*-methyl-, oil, *m*-nitro-, m.p. 70° (unchanged when kept in light petroleum in diffuse light for several days), *p*-nitro-, m.p. 128° , -3:3'-dimethyl-, oil, -3:3'-dinitro-, m.p. 144° , -4:4', -2:4', oil, and -2:6-dimethoxy-, oil, *p*-chloro-, m.p. 32° (cf. loc. cit.), *p*-bromo-, m.p. 39° , and *p*-iodo-, m.p. 62° , -azobenzenes and *cis*-benzeneazo- α -naphthyl Me ether, m.p. 70° . The *cis*-configuration is based on analogy with previous examples and the easy reversion to the *trans*-form on fusion. They show varying degrees of stability in inert solvents at room temp. in the dark; the electronic nature of the substituents is insufficient to account for the differences. Short irradiation only is necessary for *cis-trans* equilibrium in solid *m*-nitroazobenzene and the *cis*-form is obtained directly (in appreciable amounts) from crude or old preps. by adsorption. $p-NO_2 \cdot C_6H_4 \cdot NH_2$ (I) in C_6H_6 with aq. NaOCl gives (cf. Meigen *et al.*, A., 1900, i, 702)

4 : 2 : 6 : 1- $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NH}_2$ and a *tetrachloro-4 : 4'-dinitroazobenzene*, m.p. 267° , or (shorter reaction time) 2 : 2'-dichloro-4 : 4'-dinitroazobenzene and a ? *dichloro-4 : 4'-dinitroazobenzene*, m.p. 144° . 4 : 4'-Dinitroazobenzene* is obtained from (I) and $\text{K}_2\text{S}_2\text{O}_8$ in aq. H_2SO_4 at $60-70^\circ$. It is unlikely that α - and β -4 : 4'-dihydroxyazobenzene hydrates are *cis-trans*-isomerides (cf. Willstätter *et al.*, A., 1907, i, 566) since they are unchanged (spectra) after prolonged irradiation; they both give the α -hydrate on fusion, yield a mixture of the green and orange forms of the anhyd. α -compound when distilled at $170^\circ/0.002$ mm., afford the same *picrate* ($+\text{H}_2\text{O}$), m.p. 183° , appear to give the same diacetate, and are methylated (Me_2SO_4 or CH_2N_2) to *trans-4 : 4'-dimethoxyazobenzene*. 2-Hydroxy-2'-methoxy-, m.p. 110° , and 2 : 2'-dimethoxy*-azobenzene are formed by successive treatment of the $(\text{OH})_2$ -derivative with Me_2SO_4 -aq. NaOH . The isomerism of *p*-hydroxybenzenesazophloroglucinol is physical; both forms with CH_2N_2 give the same *Me* ether, m.p. 118° . The *trans-Me* ether, m.p. 94° , of 1-*o*-iodobenzenesazo- β -naphthol, m.p. 176° , affords a labile isomeride, as does 2-methoxy-2'-methyl-1 : 1'-azobenzene, m.p. 72° (from 2 : 1- $\text{C}_{10}\text{H}_7\text{Me} \cdot \text{N}_2\text{Cl}$ and β - $\text{C}_{10}\text{H}_7\text{OH}$ with subsequent methylation). Reduction (Na_2SnO_2) of *o*- $\text{C}_6\text{H}_4\text{I} \cdot \text{NO}_2$ gives 2 : 2'-di-iodoazobenzene, m.p. 148° , which with 4% Na-Hg in EtOH-OMe_2 followed by a little H_2O_2 affords $(\text{NPh})_2$. Irradiation of *p*- $\text{C}_6\text{H}_4(\text{N} \cdot \text{NPh})_2$ (to which is ascribed a *trans-trans*-configuration) gives (probably) the *cis-trans*-isomeride, m.p. 136° , and *cis-cis*-form; *cis-cis*- and *cis-trans-4 : 4'-bisbenzenesazodiphenyls* are similarly obtained. 4 : 4'-Bis(benzenesazo)azobenzene appears to give at least one isomeride. *trans*-Benzenesazo- β -naphthyl *Me* ether, *o*-nitro- and 2 : 2'-dinitro-azobenzene, and compounds marked * are unaffected by irradiation.

The 3 : 3'-azotoluene of A., 1938, II, 317 is the 2 : 2'-compound and the compound, $\text{C}_{14}\text{H}_{14}\text{ON}_2$, is *trans-2 : 2'-azoxytoluene*. H. B.

Azo-chromophore. VIII. J. S. P. BLUMBERGER (Chem. Weekblad, 1939, 36, 574—578; cf. A., 1938, II, 180).—Spectroscopic data on a large no. of *o*-hydroxy- or -amino-azo dyes show that negative substituents in the *m*-position usually have a hypsochromic effect in acid and a bathochromic effect in alkaline media. The effect is usually intensified in presence of *o*-OMe groups but in some cases the effects neutralise one another. The total effect is approx. the algebraic sum of the effects of each substituent separately. The tendency to dissociation of the proton is decreased by the introduction of positive groups into the azo-chromophore and increased by introduction of negative groups in the *m*- or *p*-positions. The effects are explained by the $\pi 2p$ -electron shell of the $\text{N} \cdot \text{N} \cdot$ group assuming a higher quantum level, which predominates over the negative effect expected from the suppression of polarisation.

S. C.

Azo-dyes from naphthidine (4 : 4'-diamino-1 : 1'-dinaphthyl). P. P. T. SAH and K. H. YUIN (Rec. trav. chim., 1939, 58, 751—757).—Azo-dyes are obtained from tetrazotised naphthidine and the following components (2 mols.): *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$

(orange-yellow on wool and cotton), 4 : 1- $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$ (red on wool, silk, and cotton), 2 : 6- $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{H}$ (violet-red on wool and silk, violet on cotton), *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ (brownish-red on wool, yellow-orange on silk, red-violet on cotton), 1-phenyl-3-methyl-5-pyrazolone (orange on cotton).

J. D. R.

Phenyl phosphoric esters. E. J. KING and T. F. NICHOLSON (Biochem. J., 1939, 33, 1182—1184).—Mol. proportions of a phenol and POCl_3 react rapidly in $\text{C}_6\text{H}_5\text{N}$ without prolonged heating. The prep. is described by this means of $\text{Na}_2\text{P}_2\text{O}_7$, $\text{BaPhPO}_4(+2\text{H}_2\text{O})$, *Ba o-tolyl* ($+1\text{H}_2\text{O}$), *Ba p-bromophenyl*, *Ba p-nitrophenyl*, and *K_2 cyclohexyl phosphate*.

P. G. M.

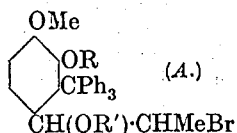
Terphenyl series. II. Hydroxy- and methyl-p-terphenyls. H. FRANCE, I. M. HELLBRON, and D. H. HEY (J.C.S., 1939, 1283—1287; cf. A., 1938, II, 437, for nomenclature).—*p*- $\text{C}_6\text{H}_4\text{Ph} \cdot \text{N} \cdot \text{Ac} \cdot \text{NO}$ (I) and *PhOMe* at 18° for 48 hr. give 2- (II) and 4- (III) -methoxy-*p*-terphenyl, m.p. $118-119^\circ$ and $223-224^\circ$, respectively, demethylated (HI) to 2- (IV) and 4-hydroxy-*p*-terphenyl, m.p. $176-177^\circ$ and $264-265^\circ$ (sublimes partly at 260°), respectively. 2-Amino-*p*-terphenyl is converted (diazo-method) into (IV), which is methylated (MeI , EtOH-KOH) to (II). 4'-Acetamido-4-methoxydiphenyl with nitrous fumes in $\text{AcOH-Ac}_2\text{O}$ at $8^\circ/2$ hr. affords the *N-NO*-derivative, detonates at 103° , which with C_6H_6 yields (III). *p*- $\text{C}_6\text{H}_4(\text{OMe})_2$ (IV) and (I), first at $50-55^\circ$ and then up to 90° , give 2 : 5-dimethoxy-, new m.p. $159-160^\circ$, and thence 2 : 5-dihydroxy-*p*-terphenyl, new m.p. $173-174^\circ$. *p*- $\text{C}_6\text{H}_4(\text{N} \cdot \text{Ac} \cdot \text{NO})_2$ (V) and (IV) similarly afford 2 : 5 : 2'' : 5''-tetramethoxy-*p*-terphenyl, m.p. $159-160^\circ$. Attempted nitrosation of 2-methoxy- NN' -diacetyl-*p*-phenylenediamine, m.p. $220-222^\circ$, in $\text{AcOH-Ac}_2\text{O-P}_2\text{O}_5$ at 8° gives the 5- NO_2 -derivative, m.p. $258-259^\circ$. *PhMe* and (I) give 2- (VI), m.p. $91-92^\circ$, and 3-, m.p. $169-170^\circ$, -methyl-*p*-terphenyl together with the 4-isomeride (VII), m.p. $207-208^\circ$. 4-Nitrosoacetamido-2'- and -4'-methylidiphenyl with C_6H_6 afford (VI) and (VII), respectively, which are oxidised (CrO_3 , dil. AcOH) to ? 2-methylidiphenyl-4-, m.p. $173-175^\circ$, and *p*-terphenyl-4-carboxylic acid, respectively. 4-Nitro-2'- and -4'-methylidiphenyl are prepared from *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$, *PhMe*, and aq. NaOH . *p*-Xylene and (V) at $50-55^\circ$ and then 90° give 2 : 5 : 2'' : 5''-tetramethyl-*p*-terphenyl, m.p. $112-113^\circ$.

H. B.

Attempted applications of camphor oil. I. Diphenylmethyl derivatives of isochavibetol. I. E. FUNAKUBO and G. KAWASAKI (Ber., 1939, 72, [B], 1518—1523).—*isoChavibetol* and CHPh_2Cl in $\text{C}_5\text{H}_5\text{N}$ at 150° give *isochavibetol CHPh}_2* ether (I), m.p. $105-106^\circ$, *diphenylmethylisochavibetol* (II), m.p. $154.8-155.8^\circ$, and its *CHPh}_2* ether, m.p. $160-161^\circ$. After 20 hr. the yields of (I) and (II) are equal; if heating is more prolonged the yield of (I) declines rapidly whereas that of (II) increases to a max. after 50 hr. (II) yields an *acetate*, m.p. $122.7-123.2^\circ$, a *Me* ether, m.p. $115.5-116.5^\circ$, and a *dibromide* (III), m.p. $160-160.5^\circ$. (III) is converted by the requisite alcohol or by AcOH into β -bromo- α -methoxy-, m.p. $161-165^\circ$, - α -ethoxy-, m.p. $124.2-126.2^\circ$, and - α -acetoxy-, m.p.

153.7—154.8° (decomp.), *-diphenylmethyldihydroisochavibetol*. (II) is unchanged by KOH in aq. EtOH at 200—238°. H. W.

Introduction of the triphenylmethyl group. VII, VIII. Mobility of the bromine atom in triphenylmethylisochavibetol and in its derivatives. III, IV. E. FUNAKUBO and T. HIROTANI (Ber., 1939, 72, [B], 1513—1515, 1516—1517).—VII. Triphenylmethylisochavibetol dibromide (I) is converted by boiling aq. COMe_2 into β -bromo- α -hydroxytriphenylmethyldihydroisochavibetol ($A, R = R' = H$), m.p. 187° (decomp.), the structure of which is proved by its inability to give CHI_3 when oxidised with I in alkaline solution.



The following β -bromo- α -hydroxytriphenylmethyldihydroisochavibetol alkyl ethers ($A; R = \text{alkyl}; R' = H$) are described: *Me*, m.p. 164° (decomp.); *Et*, m.p. 164—165° (slow decomp.); *Prⁿ*, m.p. 168—169° (slow decomp.); *Prⁱ*, m.p. 159—160° (slow decomp.); *Buⁿ*, m.p. 139—140°; *Buⁱ*, m.p. 134—135° after becoming opaque at 124—127° [formed with a substance (? *Buⁿ* ether), $\text{C}_{33}\text{H}_{35}\text{O}_3\text{Br}$, m.p. 124° (slow decomp.) after becoming opaque at 114°]; *isoamyl*, m.p. 155—157° (slow decomp.).

VIII. (I) is converted by the requisite hot alcohol into the corresponding β -bromo- α -alkoxytriphenylmethyldihydroisochavibetol [$A, R = H; R' = \text{Prⁿ}$, m.p. 160—161° (slow decomp.); *Prⁱ*, m.p. 159—160° (slow decomp.); *Buⁿ*, m.p. 145—146° (slow decomp.); *Buⁱ*, m.p. 160° (slow decomp.); *Buⁿ*, m.p. 179—180° (decomp.); *n-amyl*, m.p. 159—160°; *isoamyl*, m.p. 116°; *n-hexyl*, m.p. 135—137°]. H. W.

Duroquinol monophenyl ether.—See B., 1939, 997.

Bromination of 2-methoxydiphenyl ether. F. LIONS and A. M. WILLISON (J. Proc. Roy. Soc. New South Wales, 1939, 72, 257—272).—Gradual addition of Br in AcOH to *o*- $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ in AcOH gives 5-bromo- (I), m.p. 71°, 5:4'-dibromo- (II), m.p. 64°, and 4:5:4'-tribromo-, m.p. 131°, -2-methoxydiphenyl ether. If the AcOH solution after bromination is heated at 75° for several hr., the OMe is partly hydrolysed and the phenols thus formed may be removed from the oily reaction product by extraction of its solution in Et_2O by alkali hydroxide; 2-hydroxydiphenyl ether, m.p. 106°, and 5-bromo-2:3':5'-dinitrobenzoyloxydiphenyl ether, m.p. 102°, are thus isolated. Further amounts of (I) can be obtained as the unchanged portion when oily residues from the bromination are nitrated. The synthesis of (I) from 5:2:1- $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OPh}$ is recorded; 4'-bromo-2-methoxydiphenyl ether (III), b.p. 195—197°/15 mm., m.p. 38°, is obtained from the 4'- NH_2 -compound. 5-Bromo-4'-amino-2-methoxydiphenyl ether (IV) has m.p. 88° (lit. 105°). (II) is readily obtained by the action of a larger proportion (see above) of Br in AcOH on *o*- $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, by bromination of *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ in AcOH, or by Gattermann's method from (IV). 5:2:1- $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OPh}$ is brominated to (?) 5-acetbromoamido-2-methoxydiphenyl ether, highest observed m.p. 158° (decomp.), readily transformed by aq. or hydroxylic solvents into

4-bromo-5-acetamido-2-methoxydiphenyl ether, m.p. 100°, which is hydrolysed by boiling 15% KOH-MeOH to the 5- NH_2 -derivative, m.p. 68°, converted (diazo-method) into 4:5-dibromo-2-methoxydiphenyl ether, b.p. 230—232°/15 mm., m.p. 83°. 5-Bromo-4:4'-dinitro-2-methoxydiphenyl ether, m.p. 170°, is obtained by the action of fuming HNO_3 on (I) in $\text{AcOH}\cdot\text{Ac}_2\text{O}$, from (I) and warm HNO_3 (d 1.42), and from 5-bromo-4-nitro-2-methoxydiphenyl ether and HNO_3 (d 1.5) in $\text{AcOH}\cdot\text{Ac}_2\text{O}$; it is readily converted into 4:4'-dinitro-5-morpholyl-2-methoxydiphenyl ether, m.p. 191°. 4'-Bromo-5-nitro-2-methoxydiphenyl ether, m.p. 150°, is prepared by bromination of 5:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OPh}$ or from HNO_3 (d 1.42) and (III). 4:2:1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OPh}$ has m.p. 59°. H. W.

Aminoaryl alkyl sulphones.—See B., 1939, 916.

Epimeric alcohols of the cyclohexane series. II. 4-Methyl- and 4-isopropyl-cyclohexylcarbinols. R. G. COOKE and A. K. MACBETH (J.C.S., 1939, 1245—1247).—*p*- $\text{C}_6\text{H}_4\text{Pr}^i\cdot\text{CO}_2\text{H}$ is reduced by H_2 -PtO₂ in warm AcOH to *cis*-hexahydrocuminic acid, b.p. 133°/2.5 mm. (*Et*, b.p. 94°/2.5 mm., *p*-chlorophenacyl, m.p. 61°, and *p*-bromophenacyl, m.p. 85°, esters), and by H_2 -Raney Ni in 10% NaOH at 200°/150—200 atm. to *trans*-hexahydrocuminic acid (*Et*, b.p. 100°/2 mm., *p*-chlorophenacyl, m.p. 97.5°, and *p*-bromophenacyl, m.p. 108°, esters); *cis*- and *trans*-hexahydro-*p*-toluic acids (*Et*, b.p. 64°/3 mm., and 71°/2 mm., respectively, *p*-chlorophenacyl, m.p. 90° and 105°, respectively, and *p*-bromophenacyl esters, m.p. 100° and 135°, respectively) are similarly prepared. Hydrogenolysis (H_2 , Cu-Ba-Cr oxide, 250°/~200 atm.) of the appropriate *Et* ester gives *cis*-4-methylcyclohexylcarbinol, b.p. 75°/2.5 mm. (*H* phthalate, m.p. 127°; α -naphthylcarbamate, m.p. 72—73°), *trans*-4-methylcyclohexylcarbinol, b.p. 74°/3 mm. (*H* phthalate, m.p. 147—148°; *p*-nitrobenzoate, m.p. 57°; 3:5-dinitrobenzoate, m.p. 112°; phenylcarbamate, m.p. 82.5°; α -naphthylcarbamate, m.p. 110.5°), *cis*-4-isopropylcyclohexylcarbinol, b.p. 101°/2 mm. (*H* phthalate, m.p. 107—108°; *p*-nitrobenzoate, m.p. 54—55°; 3:5-dinitrobenzoate, m.p. 72°; α -naphthylcarbamate, m.p. 72—73°), and *trans*-4-isopropylcyclohexylcarbinol, b.p. 98°/2 mm. (*H* phthalate, m.p. 107—108°; *p*-nitrobenzoate, m.p. 47.5°; 3:5-dinitrobenzoate, m.p. 95°; phenylcarbamate, m.p. 74°; α -naphthylcarbamate, m.p. 93°). Physical consts. are in agreement with the Auwers-Skita rule. The *cis*-alcohols are contaminated by small amounts of the *trans*-compounds, which are readily obtained pure through the *H* phthalates. H. B.

Phenylpropoxyethyl alcohol. A. HALASZ (Compt. rend., 1939, 209, 319—321; cf. A., 1939, II, 155).— β -(γ -Phenylpropoxy)ethyl alcohol (I) has a somewhat greater solubility in H_2O and a lower η than $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{OH}$. (I) is stable to dil. acid or alkali, but with Cr_2O_3 , H_2O_2 , or PbO it yields $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CHO}$, MeCHO , and the corresponding acids. (I) with HI (Zeisel) gives *EtI* (39% yield). The following are prepared by the usual methods: β -(γ -phenylpropoxy)ethyl formate, b.p. 161—162°/18 mm., propionate, b.p. 140—141°/1 mm., isobutyrate, b.p. 154—155°/3 mm., benzoate, b.p. 204—205°/4

mm., *chloride*, b.p. 146—147°/18 mm., *bromide*, b.p. 155—156°/15 mm., and *iodide*, b.p. 171—172°/19 mm., *Me*, b.p. 134—136°/20 mm., *Et*, b.p. 141—143°/18 mm., *Pr*, b.p. 154—155°/20 mm., *benzyl*, b.p. 183—185°/1 mm., *triphenylmethyl*, m.p. 80—80.5°, and ? *β-hydroxyethyl ether*, b.p. 190—192°/18 mm.

J. L. D.

cis- and trans-1- and -dl-3-Methylcyclopentanol. I—IV. M. GODCHOT, (Mlle.) G. CAUQUIL, and R. CALAS (Bull. Soc. chim., 1939, [v], 6, 1353—1358, 1358—1365, 1366—1370, 1370—1374).—I. *d*-β-Methyladipic acid in Ac_2O at $>170^\circ$ yields *d*-3-methylcyclopentanone (I), new (higher) $[\alpha]_{\text{D}}^{20} +152.84^\circ$.

II. With H_2 -Pt (Adams) in AcOH , (I) gives *cis*-1-3-methylcyclopentanol (II), b.p. 60°/15 mm., $[\alpha]_{\text{D}}^{20} -6.55^\circ$ [*H phthalate*, non-cryst.; *p*-nitrobenzoate (III), m.p. 37°; $[\alpha]_{\text{D}}^{21} +4.88^\circ$ in MeOH ; *phenylurethane*, m.p. 78°, $[\alpha]_{\text{D}}^{21} +0.92^\circ$ in EtOH ; *acetate*, b.p. 61.5°/16 mm., $[\alpha]_{\text{D}}^{20} -0.42^\circ$]. With Na in aq. Et_2O , (I) gives *trans*-1-3-methylcyclopentanol (IV), b.p. 62.5°/15 mm., $[\alpha]_{\text{D}}^{20} -6.50^\circ$ [*H phthalate*, non-cryst.; *p*-nitrobenzoate (V), m.p. 41°; $[\alpha]_{\text{D}}^{21} +0.65^\circ$ in MeOH ; *phenylurethane*, m.p. 82°, $[\alpha]_{\text{D}}^{21} +0.62^\circ$ in EtOH ; *acetate*, b.p. 63°/15 mm., $[\alpha]_{\text{D}}^{20} -0.95^\circ$]. The *cis*- and *trans*-structures are assigned because (V) is hydrolysed more rapidly than (III), and (IV) is more viscous than (II). Both (II) and (IV) are oxidised (CrO_3 - AcOH) to (I).

III. *dl*-β-Methyladipic acid heated with 5% BaCO_3 gives *dl*-3-methylcyclopentanone (VI), which with H_2 -Pt gives *cis*-*dl*-3-methylcyclopentanol (VII), b.p. 65°/23 mm. (cf. A., 1913, i, 873) [*p*-nitrobenzoate (VIII), m.p. 70°; *phenylurethane*, m.p. 80°]. With Na in aq. Et_2O , (VI) gives (VII) and its *trans*-isomeride (IX), b.p. 70°/24 mm. [*p*-nitrobenzoate (X), m.p. 44°; *phenylurethane*, m.p. 78°]. Both (VII) and (IX) are oxidised to (VI).

IV. The rates of hydrolysis of (III), (V), (VIII), and (X), with other physical data on the above isomerides, are tabulated. E. W. W.

Isolation of phenol dialcohols from reaction mixtures. F. SEEBACH (Ber., 1939, 72, [B], 1635—1638).— MgO slowly dissolves in a cold mixture of PhOH and 30% CH_2O and after a further period the compound, $(\text{C}_6\text{H}_5\text{O}_3)_2\text{Mg}\cdot\text{H}_2\text{O}$, crystallises. It is readily converted by AcOH into 1:2:6- $\text{OH}\cdot\text{C}_6\text{H}_3(\text{CH}_2\cdot\text{OH})_2$ (triacetate, m.p. 87°), the constitution of which follows from its methylation and subsequent oxidation to 2:1:3- $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$. Similarly, *m*-cresol affords the compound, $\text{C}_{18}\text{H}_{26}\text{O}_8\text{Mg}$, which yields 2:4-di(hydroxymethyl)-*m*-cresol. Similar Pb and Mn^{III} salts are formed. H. W.

Hardening process of phenol-formaldehyde resins. II. F. HANUS and E. FUCHS [with E. ZIEGLER] (J. pr. Chem., 1939, [ii], 153, 327—336).—*p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{OH}$, 10% NaOH , and 40% CH_2O at room temp. give 4-ethyl-2:6-di(hydroxymethyl)phenol (*p*-ethylphenol dialcohol), m.p. 85.8—86.6° (*Na* salt; *p*-toluenesulphonate, m.p. 130—131°). 4-*n*-Propyl-, m.p. 85.4—85.8°, -*n*-butyl-, m.p. 67—67.4°, and -*tert*-butyl-, m.p. 74—75° (*p*-toluenesulphonate, m.p. 140°), 2:6-di(hydroxymethyl)phenol are described. When these compounds are heated the amount of H_2O liberated predominates at lower and of CH_2O

at higher temp. The incidence of elimination of CH_2O appears to depend on the size of the *para*-substituent. With increasing size the stepwise elimination becomes more distinct independently of the m.p. of the dialcohol. Nearly all the compounds investigated lose H_2O at ~ 110 — 130° ; loss of CH_2O commences at a temp. which increases with the sum of the atoms in the *para*-substituent. The influence of constitution is apparent in the behaviour of the Bu^n and Bu^t compounds in which loss of H_2O and CH_2O occurs more readily from the latter, which is therefore particularly suited to the production of artificial resins. The hypothesis that the initial loss of H_2O is accompanied by the formation of ethers is supported by the observation that the product obtained from 4-cyclohexyl-2:6-di(hydroxymethyl)phenol at 140° is converted by $\text{HBr}\cdot\text{AcOH}$ into 4-cyclohexyl-2:6-di(bromomethyl)phenol, m.p. 81.8°. Analogously, 4-methyl-2:6-di(hydroxymethyl)phenyl *p*-toluenesulphonate when heated at 204° and then treated with $\text{AcOH}\cdot\text{HBr}$ yields 4-methyl-2:6-di(bromomethyl)phenyl *p*-toluenesulphonate, m.p. 122.3—122.5°. H. W.

Constituents of natural phenolic resins.

XVI. Synthesis of lignan diols. R. D. HAWORTH and D. WOODCOCK (J.C.S., 1939, 1237—1241; cf. A., 1937, II, 497).—Reduction (4% $\text{Na}\cdot\text{Hg}$) of 1:2:3- $\text{C}_{10}\text{H}_5\text{Ph}(\text{CO}_2\text{H})_2$ gives a mixture (A), m.p. 170 — 180° , of stereoisomeric 1-phenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acids; a homogeneous form (I), new m.p. 209° (decomp.) [converted by hot AcCl into an anhydride (II), new m.p. 155 — 156° , which is sulphonated by cold conc. H_2SO_4], is isolable by repeated crystallisation from COMe_3 . Alkaline hydrolysis of (II) affords an isomeride, m.p. 219° , of (I). Esterification (*Ag* salt method) of (A) gives solid (III), m.p. 106 — 109° , and liquid (IV), b.p. 190 — $195^\circ/1$ mm., Me_2 esters; boiling $\text{MeOH}\cdot\text{HCl}$ or $-\text{H}_2\text{SO}_4$ also affords (III) and (IV) after 4 hr. but (IV) only after 12 hr. The configuration of the ester is thus modified by mineral acid. Distillation of (III) also gives (IV). Bouveault-Blanc reduction of (III), (IV), or the *Et*₂ ester, b.p. 210 — $215^\circ/1.5$ mm., yields $\sim 20\%$ of 1-phenyl-2:3-di(hydroxymethyl)-1:2:3:4-tetrahydronaphthalene (probably a mixture of stereoisomeric forms), dehydrated (KHSO_4 at 180°) to a little of an *anhydro*-derivative, m.p. 103 — 104° . 6:7-Dimethoxy-1-3':4'-dimethoxyphenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid, crude, m.p. 140 — 155° , homogeneous form, m.p. 155 — 157° [Me_2 ester (+ MeOH), m.p. 110° (using MeOH -acid), m.p. (MeOH -free) 146° (from *Ag* salt)], with $\text{EtOH}\cdot\text{H}_2\text{SO}_4$ gives *EtH*, m.p. 122° , and solid, m.p. 116 — 117° , and liquid, b.p. 270 — $275^\circ/3$ mm., Et_2 esters. Reduction of the Et_2 ester affords 40% of a mixture of 6:7-dimethoxy-1-3':4'-dimethoxyphenyl-2:3-di(hydroxymethyl)-1:2:3:4-tetrahydronaphthalene; this in Et_2O slowly deposits a little of a form (V), m.p. 155 — 158° , the *anhydro*-derivative, m.p. 126 — 127° , of which is dehydrogenated by $\text{AcOH}\cdot\text{Pb}(\text{OAc})_2$ at 70° to dehydroanhydroisolariciresinol Me_2 ether [also obtained by the same procedures from the material from the mother-liquors after separation of (V)].

The oil obtained in 37% yield by reduction of the *Et*₂ ester, b.p. 260—265°/1.5 mm., of 6:7-methylenedioxy-1-3': 4'-methylenedioxyphenyl-1: 2: 3: 4-tetrahydronaphthalene-2: 3-dicarboxylic acid (inseparable mixture) similarly deposits a little 6:7-methylenedioxy-1-3': 4'-methylenedioxyphenyl-2: 3-di(hydroxymethyl)-1: 2: 3: 4-tetrahydronaphthalene, m.p. 183—184° (? 187°) (*anhydro*-derivative, m.p. 137°). Configurational change during Bouveault-Blanc reduction is confirmed by the observation that *Et*₂ meso- (VI), m.p. 114—115° (*Me*₂ ester has m.p. 136—137°), dl- (VII), oil (*Me*₂ ester, m.p. 65—66°), d-, m.p. 65—66°, $[\alpha]_D^{25} +26.4^\circ$ in CHCl_3 , and l-, m.p. 65—66°, $[\alpha]_D^{25} -26.2^\circ$ in CHCl_3 , - $\alpha\alpha'$ -di-(3: 4-dimethoxybenzyl)succinates [from the Ag salts of the respective acids (A., 1939, II, 122)] all yield an oily, inactive $\alpha\delta$ -di-(3: 4-dimethoxyphenyl)- $\beta\gamma$ -di(hydroxymethyl)butane, distils/2 mm. (*diformate*, m.p. 131—132°; *anhydro*-derivative, m.p. 118—119°), which is oxidised (NaOBr) to dl-matairesinol *Me*₂ ether. The ester not reduced also undergoes stereochemical change since, e.g., *meso*- and *dl*-acid are recovered from both (VI) and (VII). H. B.

Mobility of the cycloheptane ring and configuration of the cycloheptane-1: 2-diols. J. BÖSEKEN (Rec. trav. chim., 1939, 58, 856—862).—The results of Hermans and Maan (A., 1938, II, 320) on the steric analysis of *cis*- (I) and *trans*- (II) -cycloheptane-1: 2-diols are discussed in connexion with ring formation with H_3BO_3 by (I) and (II), and the non-formation of a ring by *cis*-cyclohexane-1: 2-diol. The phenomena observed with cyclodiol agree satisfactorily with the hypothesis of intramolecular movements of a vibratory character. J. D. R.

Molecular compounds of bile acids with sterols. IV. Cholesterol. H. RHEINBOLDT [with A. LAUBER] (Z. physiol. Chem., 1939, 260, 279—284; cf. A., 1929, 925; Partington, J.C.S., 1911, 99, 313).—M.p. curves for binary mixtures of cholesterol (I) with palmitic, stearic, stearolic, brassidic, and behenic acid show that no crystalline compounds, but possibly mixed crystals, are produced. In each case a single eutectic mixture is obtained, the m.p. and % of (I) being 56°, 25; 63.5°, 27; 44°, 14; 55°, 19; and 52°, 14 respectively. W. McC.

Reactions of α - and β -cholesteryl benzoate oxides. F. S. SPRING and G. SWAIN (J.C.S., 1939, 1356—1359).—Cholesteryl benzoate and BzO_2H in CHCl_3 at 0°/12 hr. and 20°/4 days give ~50% of α - (I), m.p. 168—169°, $[\alpha]_D^{25} -31.3^\circ$, and ~40% of β - (II), m.p. 151—152°, $[\alpha]_D^{25} +3.8^\circ$, -cholesteryl benzoate oxide, hydrolysed (EtOH-KOH) to α - (III) and β - (IV) -cholesterol oxide, respectively. 3: 5: 6-Trihydroxycholestane and BzCl (excess) in $\text{C}_5\text{H}_5\text{N}$ at 100° (bath) afford a Cl-containing gelatinous product; with $\text{Bz}_2\text{O-C}_5\text{H}_5\text{N}$ the 3-monobenzoate, m.p. 222—223°, $[\alpha]_D^{25} -4.9^\circ$ [also obtained from (I) and hot C_6H_6 -66% H_2SO_4], and (I) are produced. 6-Chloro-5-hydroxy-3-benzoyloxycholestane, m.p. 202—203° (decomp.), $[\alpha]_D^{25} -19.5^\circ$ [from (III) and $\text{BzCl-C}_5\text{H}_5\text{N}$ or (I) and $\text{EtOH-C}_6\text{H}_6\text{-HCl}$ (*d* 1.16) or $\text{CHCl}_3\text{-HCl}$], is converted by short treatment with quinoline at 180° into (I), and by $\text{SOCl}_2\text{-C}_5\text{H}_5\text{N}$ at 0° into 6-chloro-3-benzoyloxy- Δ^4 -cholestene, m.p. 127—128°, $[\alpha]_D^{25} -79.4^\circ$.

5-Chloro-6-hydroxy-3-benzoyloxycholestane, m.p. 206—207° (decomp.), $[\alpha]_D^{25} \pm 0^\circ$ [from (II) and HCl (as above)], and $\text{BzCl-C}_5\text{H}_5\text{N}$ give the 3: 6-dibenzoate, new m.p. 184°, $[\alpha]_D^{25} -68.6^\circ$, which is also formed from (II) or (IV) and $\text{BzCl-C}_5\text{H}_5\text{N}$. 6-Ketocholestanyl benzoate is obtained from (I) and anhyd. alum at 180°/0.1 mm. or P_2O_5 in boiling xylene. The (I), m.p. 181°, of Lettré *et al.* (A., 1937, II, 455) could not be prepared. $[\alpha]_D$ are in CHCl_3 . H. B.

Photochemical dehydrogenation of ergosterol and 7-dehydrocholesterol. T. ANDO (Bull. Chem. Soc. Japan, 1939, 14, 285—290).—The same ergopinacone (diacetate, new m.p. 207—207.5°) and 7-dehydrocholesterolpinacone (I), $\text{C}_{54}\text{H}_{86}\text{O}_2\cdot\text{H}_2\text{O}$, m.p. 184.5—185.5° (diacetate, new m.p. 190—190.5°; dibenzoate, m.p. 183—183.5°, obtained from 7-dehydrocholesteryl benzoate), are obtained from ergosterol and 7-dehydrocholesterol (II), respectively, when the $\text{EtOH-C}_6\text{H}_6$ -eosin solutions are freed from air either by CO_2 or by boiling (cf. Schenck *et al.*, A., 1937, II, 59) prior to insolation. Shorter exposure of (II) to sunlight appears to give ? (I), m.p. 192.5—193.5° (cf. *loc. cit.*). M.p. are corr. with decomp. S. H. H.

17-Amino- Δ^5 -androstene-, m.p. 164—166.5°, and -androstan-3-ol, m.p. 174°.—See B., 1939, 995.

Basic esters of aralkylacetic acids and their spasmolytic properties. T. WAGNER-JAUREGG, H. ARNOLD, and P. BORN (Ber., 1939, 72, [B], 1551—1561).—Muscular spasmolytic action greatly exceeding that of papaverine is observed in the β -diethylaminoethyl esters of disubstituted acetic acids. In this group, the atropine-like, neural spasmolytic effect diminishes with increasing mol. wt. Substances with high papaverine vals. have usually small atropine vals. A very favourable combination of neural and powerful muscular action is observed in β -diethylaminoethyl $\alpha\beta$ -diphenylpropionate and β -phenyl- α -isopropylpropionate. The following are described: β -diethylaminoethyl γ -phenyl- α - β' -phenylethylbutyrate, b.p. 200—210°/1 mm. (*hydrochloride*, m.p. 94—95°; *ethobromide*, m.p. 126—127°), and β -phenyl- α -benzylpropionate (*hydrochloride*, m.p. 142—144°; *octabromide*, m.p. 103—105°); γ -diethylamino-*n*-propyl, m.p. 109—111°, β -dimethylaminoethyl, m.p. 105—108°, and *tropine*, m.p. 247—249°, β -phenyl- α -benzylpropionate *hydrochloride*; β -diethylaminoethyl $\alpha\beta$ -diphenylpropionate *hydrochloride*, m.p. 111—112° (free ester, b.p. 190—195°/1 mm.); β -diethylaminoethyl β -anisyl- α -benzylpropionate, b.p. 220—230°/0.05 mm. (*hydrochloride*, m.p. 73—74°); β -diethylaminoethyl γ -cyclohexyl- α - β' -cyclohexylethylbutyrate, b.p. 220—230°/0.1 mm. (*hydrochloride*, m.p. 135—136°); β -diethylaminoethyl diphenylacetate *benzylbromide* (+ H_2O), m.p. 105—106°. All m.p. are corr. H. W.

Isomerisation of methyl allocinnamate by hydrogen bromide and the influence of oxygen. O. SIMAMURA (Bull. Chem. Soc. Japan, 1939, 14, 294—296; cf. A., 1939, II, 139).—Me allocinnamate (I) and HBr, in absence of air, in the dark at room temp., afford Me cinnamate (II), the isomerisation being slower in CCl_4 . It is accelerated by O_2 , the

action of which is suppressed by o - $C_6H_4(OH)_2$. (I) and HCl at 55° slowly afford (II), but there is no isomerisation in CCl_4 even in presence of O_2 . Piperidine also causes 34% conversion of (I) into (II) during 24 hr. S. H. H.

Condensation of aldehydes with malonic acid.

XII. Influence of groups and other factors. K. C. PANDYA, T. S. SODHI, and (in part) D. S. MITTAL (Proc. Indian Acad. Sci., 1939, 9, A, 511—517; cf. A., 1938, II, 363).—3 : 4 : 1- $C_6H_3(OH)_2$ -CHO, $-OMe$ - $C_6H_3(OH)$ -CHO, and $-C_6H_3(OMe)_2$ -CHO with $CH_2(CO_2H)_2$ (equimol. proportions) at 70 – 100° yield respectively 17, 62, and 87%, or in presence of C_5H_5N , 44, 51, and 60% yields of the corresponding cinnamic acids; with 2 mols. of $CH_2(CO_2H)_2$, C_5H_5N (6 mols.), and a trace of piperidine (I) at 10 – 25° for 3 weeks the yields are 83, 71, and [without (I)] 82% respectively. Conc. H_2SO_4 and EtOH-HCl are less effective as condensing agents. o -, m -, and p - NO_2 - C_6H_4 -CHO with $CH_2(CO_2H)_2$, alone (yield $\sim 52\%$) and in presence of C_5H_5N , (I), and quinoline (yield 75–91%), give the corresponding *trans*-nitro-cinnamic acids. A. LI.

Condensation of aldehydes. III. p -Tolualdehyde with amides. XI. p -Tolualdehyde with malonic and malonanilic acid. R. K. MEHRA and K. C. PANDYA (Proc. Indian Acad. Sci., 1939, 9, A, 508–510; cf. A., 1938, II, 363, 365).—III. p - C_6H_4Me -CHO with $HCO-NH_2$ and a trace of C_5H_5N at 175 – 180° yields *p*-tolylidenebisformamide, m.p. 287° . Other amides react at 120 – 130° with or without C_5H_5N , giving *p*-tolylidenebis-acetamide, m.p. 274° , -propionamide, m.p. 232° , -benzamide, m.p. 230° , and -phenylacetamide, m.p. 238° .

XI. p - C_6H_4Me -CHO heated with $CH_2(CO_2H)_2$ and CO_2H - CH_2 - CO -NHPh in presence of C_5H_5N yields *p*-methyl-cinnamic acid and -cinnamanilide, m.p. 184° , respectively. A. LI.

Condensation of piperonal with succinic acid derivatives. J. W. CORNFORTH, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 72, 228–232).—Piperonal (I), Ac_2O , and Na_2 succinate at 125° for 3 hr. give a mixture of 3 : 4-methylenedioxyphenyl-paraconic (II), m.p. 164 – 165° , and -isocrotonic acid (III), m.p. 117 – 118° . When heated above its m.p. (II) gives (III) and CO_2 quantitatively. Pyrolysis of (III) at 260° under atm. or somewhat diminished pressure, prolonged boiling of (III) with Ac_2O , or treatment with $POCl_3$ at 100° gives intractable tars or unchanged material. (I), Et_2 succinate, and $NaOEt$ in hot EtOH afford 3 : 4-methylenedioxyphenylitaconic acid (IV), m.p. 194 – 195° , in 90% yield, also obtained less advantageously from Zn turnings, (I), and Et_2 bromosuccinate in dry C_6H_6 ; its *Et H* ester, long needles or rhombic plates, m.p. 130 – 131° , is pyrolysed in "calol" at 290° to C_2H_4 and (IV). H. W.

Effect of polar groups on esterification velocities of substituted benzoic acids with cyclohexanol.—See A., 1939, I, 529.

Reaction of 3 : 5-dinitrobenzoic acid with alkali. I. Isolation and constitution of the compound giving a red colour with alkali. A.

BOLLIGER and F. REUTER (J. Proc. Roy. Sci. New South Wales, 1939, 72, 329–334).—Exposure of a mixture of 3 : 5 : 1- $(NO_2)_2C_6H_3$ - CO_2H and $12N$ -NaOH at 40° to the light of a 75-w. lamp, particularly in presence of traces of heavy metals such as Fe, gives a 10% yield of 5-nitro-2 : 3-dihydroxybenzoic acid, m.p. 223 – 224° [K (+ $3H_2O$) (I) and NH_4 (II) salts]. (I) in $2N$ -NaOH with Me_2SO_4 gives 5-nitro-3-methoxysalicylic acid, m.p. 220° , and its *Me* ester, m.p. 138 – 139° . (II) is transformed by CaO at $250^\circ/20$ mm. into 4 : 2 : 1- NO_2 - $C_6H_3(OH)_2$. H. W.

Alkaline hydrolysis of ethyl anthranilate.—See A., 1939, I, 527.

Theory of allyl isomerisation. III. O. MUMM and J. DIEDERICHSEN (Ber., 1939, 72, [B], 1523–1527).—The product obtained (A., 1939, II, 113) by the isomerisation of *Me* 2- Δ^2 -pentenyl-oxy- and 2- α -ethylallyloxy-*m*-toluate is shown to be *Me* 2-hydroxy-5- Δ^2 -pentenyl-*m*-toluate. This is hydrolysed and decarboxylated to 5- Δ^2 -pentenyl-*o*-cresol (I), the *Me* ether, b.p. $140^\circ/12$ mm., of which is ozonised to 4-methoxy-3-methylphenylacetaldehyde (semicarbazone, m.p. 162°). Similarly (I) is transformed into its acetate, which is ozonised to 2-methyl-4-aldehydomethylphenoxycetic acid [semicarbazone, m.p. 184° (decomp.)]. H. W.

Syntheses in the phenylcyclohexane series. D. BODROUX and R. THOMASSIN (Bull. Soc. chim., 1939, [v], 6, 1411–1416).—Phenylcyclohexane (I) treated slowly with Br in presence of I gives *p*-bromophenylcyclohexane (II) (80% yield), new b.p. 153 – $155^\circ/10$ mm. (cf. Truffault, A., 1938, II, 476), the Mg derivative (III) of which is converted by solid CO_2 , followed by dil. HCl, into *p*-cyclohexylbenzoic acid, and by $CH(OEt)_3$ into 53% of *p*-cyclohexylbenzaldehyde (anil, new m.p. 117 – 118° ; cf. von Braun *et al.*, A., 1933, 1283). The last is also obtained by action of boiling aq. $Cu(NO_3)_2$ or $Pb(NO_3)_2$ on a saline emulsion of *p*-cyclohexylbenzyl chloride (IV), b.p. 162 – $164^\circ/12$ mm. [from (I), $(CH_2O)_3$, and HCl, in presence of $ZnCl_2$]. A by-product in the prep. of (III) is 4 : 4'-dicyclohexyldiphenyl, m.p. 202 – 203° , not obtained from (II) and Na in Et_2O or Bu^a_2O . With Na in Et_2O (IV) gives 4 : 4'-dicyclohexyl- $\alpha\beta$ -diphenylethane, m.p. 148 – 149° , which is also a by-product in the prep. from (IV) of its Mg derivative (V). In Et_2O , (V) gives, with air, *p*-cyclohexylbenzyl alcohol, and with CO_2 , slowly *p*-cyclohexylphenylacetic acid, m.p. 78 – 75° , which is oxidised by alkaline $KMnO_4$ to *p*- $C_6H_4(CO_2H)_2$. E. W. W.

Synthesis of 1 : 12-dimethyl-7-isopropylcyclohexophenanthrene-1-carboxylic acid. R. D. HAWORTH and R. L. BARKER (J.C.S., 1939, 1299–1303).—The product from *Et* 2-methylcyclohexanone-2-carboxylate and Et_2O - CH_2Ph - CH_2 -MgBr (I) is dehydrated ($KHSO_4$) to *Et* 1- β -phenylethyl-2-methyl- Δ^6 -cyclohexene-2-carboxylate, b.p. 160 – $163^\circ/3$ mm. (free acid, m.p. 97 – 98°), converted by boiling $AcOH$ -conc. H_2SO_4 into 1-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-1-carboxylic acid, m.p. 187 – 188° , which, like its *Me* ester, m.p. 75 – 76° , is dehydrogenated (Se at 280 – 290° and then 320°) to 1-methylphenanthrene (II). *Et* 2 : 6-dimethylcyclohexanone-2-

carboxylate (III), b.p. 111—112°/15 mm. (from the 6-Me derivative, EtOH—NaOEt, and MeI), and (I) similarly give *Et* 1- β -phenylethyl-2 : 6-dimethyl- Δ^6 -cyclohexene-2-carboxylate, b.p. 175—180°/4 mm. (free acid, m.p. 121—122°), cyclised (best with AcOH—H₂SO₄) to 1 : 12-dimethyloctahydrophenanthrene-1-carboxylic acid, m.p. 232—233° [*Me* ester, m.p. 128—129°, dehydrogenated to (II)]. *m*-C₆H₄Pr ^{β} ·MgBr and (CH₂)₂O at 15° (in Et₂O) and then at 100° (no Et₂O) give β -m-isopropylphenylethyl alcohol, b.p. 134—138°/20 mm. The Grignard reagent from the bromide, b.p. 130—132°/20 mm., with (III) affords (after dehydration) *Et* 1- β -m-isopropylphenylethyl-2 : 6-dimethyl- Δ^6 -cyclohexene-2-carboxylate, b.p. 173—180°/20 mm., cyclised to 1 : 12-dimethyl-7-isopropyloctahydrophenanthrene-1-carboxylic acid (IV), m.p. 202—203° (*Me* ester, m.p. 91—92°), which is dehydrogenated (Se) to retene. The absorption spectrum of (IV) resembles that of dehydroabietic acid (V); (IV) may be *dl*-(V) or a diastereoisomeride. Prep. of PhPr ^{β} from C₆H₆, Pr ^{β} Br, and AlCl₃ is improved. *p*-C₆H₄Pr ^{β} ·NHAc and Br·AcOH at 55—60° give 3-bromo-4-acetamidocumene, m.p. 129—130°, hydrolysed (EtOH—conc. HCl) to the 4-NH₂-derivative, b.p. 139—141°/20 mm., which is deaminated (diazonium sulphate in aq. EtOH with Cu-bronze) to *m*-bromocumene, b.p. 94—96°/20 mm. [oxidised (KMnO₄) to *m*-C₆H₄Br·CO₂H]. H. B.

Complex phthalates. G. J. BURROWS and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1939, 72, 175—178).—Cu(OH)₂ and Co(OH)₂ dissolve almost quantitatively in hot dil. *o*-CO₂H·C₆H₄·CO₂Na (I) giving thermostable solutions which yield the complex salts, Na₂[C₆H₄(CO₂)₂Cu(CO₂)₂C₆H₄]₂·2H₂O and Na₂[C₆H₄(CO₂)₂Co(CO₂)₂C₆H₄]₂·2H₂O, which are stable in air but are readily decomposed by dil. acids or alkalis. Ni(OH)₂ dissolves readily in dil. (I) to a complex Ni phthalate which is stable in solution but breaks up at the point of crystallisation into C₆H₄(CO₂Na)₂ and C₆H₄(CO₂)₂Ni. Very unstable solutions of a complex Cr salt are obtained by dissolving Cr(OH)₃ in hot dil. (I) or by adding an excess of C₆H₄(CO₂Na)₂ to a Cr⁺⁺⁺ salt. The complex Fe⁺⁺⁺ salt is decomposed when the solution is warmed or concentrated. Hg, Al, and Sn⁺⁺⁺ show no tendency towards formation of complex phthalates. H. W.

Metabolic products of *Aspergillus ochraceus*.

III. Synthesis of isochracin. T. TAMURA (J. Agric. Chem. Soc. Japan, 1939, 15, 685—689; cf. A., 1935, 619).—3 : 1 : 2-NO₂·C₆H₃(CO₂)₂O heated with (EtCO)₂O and EtCO₂Na yields 3-nitro- α -ethylidene-phthalide, which with dil. NaOH gives 6-nitro-2-propionylbenzoic acid. This is reduced by Na—Hg to 6-amino-2- α -hydroxypropylbenzoic acid, which on treatment with HCl is converted into 3-amino- α -ethyl-phthalide. 3-Hydroxy- α -ethylphthalide, identical with isochracin, is obtained from this by the diazo-reaction. Similarly 3 : 1 : 2-OMe·C₆H₃(CO₂)₂O yields (probably) 6-methoxy- α -ethylidenephthalide and -ethyl-phthalide, m.p. 58°. J. N. A.

Lichen substances. XCIV. Occurrence of the telephoric acid in lichens. Y. ASAHINA and S. SHIBATA (Ber., 1939, 72, [B], 1531—1533).—Continuous extraction of *Lobaria retigera*, Trev., with hot

COME₂ gives telephoric acid (I), C₂₀H₁₂O₉·H₂O, m.p. >350°, further identified by conversion by boiling Ac₂O containing a drop of conc. H₂SO₄ into the triacetate, decomp. 330°, and by Zn dust, NaOAc, and Ac₂O into leuco-telephoric acid penta-acetate, m.p. >340° after becoming brown at 320°. (I) is also obtained from *Thelephora palmata*. H. W.

Structure of bile acids and their colour reactions. Benzaldehyde test for hyo- and anthro-po-deoxycholic acid. G. SABA (J. Biochem. Japan, 1939, 29, 371—375).—Colour reactions for 33 bile acids are tabulated and correlated with the structure of the acids. The differentiation of hyo- and anthro-po-deoxycholic acid by a modified PhCHO test of Shimada (A., 1938, II, 365) is described.

F. O. H.

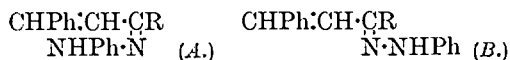
Choleic acids. V. Choleic acids containing aliphatic hydrocarbons. H. RHEINBOLDT [with P. BRAUN, E. FLUME, O. KÖNIG, and A. LAUBER] (J. pr. Chem., 1939, [ii], 153, 313—326).—Choleic acids from the following hydrocarbons and deoxycholic acid (mol. proportions in parentheses) are described : *n*-undecane (I) (1 : 6), m.p. 183°; *n*-dodecane (II), m.p. 184—185°; *n*-tridecane (III), m.p. 186°; *n*-tetradecane (IV), m.p. 188°; *n*-pentadecane (V) (1 : 8), m.p. 189.5—190°; *n*-hexadecane (VI) (1 : 8), m.p. 191.5—192°; *n*-pentatriacontane (VII) (1 : 8), m.p. ~201.5°; *n*-tritetracotane (VIII) (1 : 8), m.p. ~201°; Δ^7 -*n*-hexadecene (IX), (1 : 8), m.p. 190°; Δ^7 -*n*-heptacosene (X) (1 : 8), m.p. 195.5—196.5°; *n*-hexadecylbenzene (1 : 8), m.p. 189—189.5°. apoCholic acid affords similar compounds with (I), m.p. 181.5°; (II), m.p. 183°; (III), m.p. 185°; (IV), m.p. 187°; (V), m.p. 188.5—189°; (VI) (1 : 8), m.p. 190—190.5°; (VII) (1 : 8), m.p. ~194°; (VIII) (1 : 8), m.p. ~195°; (IX) (1 : 8), m.p. 189.5—190°; (X) (1 : 8), m.p. 194°. *p*-hydroxyphenyl-*n*-octadecane (1 : 8), m.p. 171°. (VIII) does not appear to form a compound with picric acid. H. W.

Manufacture of aldehydes.—See B., 1939, 918.

Exchange of amine residues in the internally complex salts of Schiff's bases. P. PFEIFFER and H. GLASER [with E. MILZ] (J. pr. Chem., 1939, [ii], 153, 265—284).—In the *o*-OH·C₆H₄·CHO series the imine residues are replaceable readily in the direction of the arrows : :NPh \rightarrow :NMe \rightarrow *o*-C₆H₄(N₂)₂ \rightarrow C₂H₄(N₂)₂ but not in the reverse direction. The same series is met among 2 : 1-OH·C₁₀H₆·CHO compounds except that :NPh and :NMe are mutually interconvertible. These results combined with those on the replaceability of the central metallic atom show that the tricyclic Cu salicylaldehyde-ethylenedi-imine is the most stable compound of the series. Addition of aq. Cu(OAc)₂ to *o*-OH·C₆H₄·CHO and 25% NH₂Me in MeOH at 60° yields Cu salicylaldehydemethylimine, green needles, m.p. 158° (also +1C₅H₅N); in an individual, non-reproducible experiment the compound was isolated as brown leaflets which pass into the green needles when mixed with CHCl₃ and cannot be used as seed material for further quantities of the brown compound. Cu salicylaldehydeanil has m.p. 234—236°. The exchange experiments are performed by mixing the requisite salt and an excess of amine in boiling alcohol. Addition of 50% aq. (CH₂·NH₂)₂ to a

suspension of Cu 2-hydroxy-1-naphthaldehyde in MeOH yields Cu 2-hydroxy-1-naphthaldehyde-ethylene-di-imine, m.p. $>250^\circ$. The corresponding -propylene-di-imine, -o-phenylenedi-imine, m.p. $>250^\circ$, -imine, m.p. $246\text{--}248^\circ$, -methylinimine, brown and green forms, m.p. $233\text{--}234^\circ$, -ethylimine, -benzylimine, and -anil, m.p. $237\text{--}238^\circ$, are described. H. W.

Phototropism of semicarbazones and phenylhydrazones of ethylenic ketones. IV. C. V. GHEORGHIU and V. MATRI (Bull. Soc. chim., 1939, [v], 6, 1324—1334; cf. A., 1934, 656, 774).—Styryl ketones give non-phototropic (pyrazoline-forming) and phototropic phenylhydrazones, to which the *syn*- (A) and *anti*- (B) -structures are attributed respectively,



with similar structures for isomeric semicarbazones. COMeBu⁶ and piperonal in EtOH-NaOH give 3:4-methylenedioxystryryl Bu⁶ ketone, m.p. $64\text{--}65^\circ$. This gives two isomeric semicarbazones, α (I),* m.p. $190\text{--}191^\circ$, and γ (II),* m.p. $190\text{--}191^\circ$; a δ -phenylsemicarbazone,* m.p. 185° ; and a phenylhydrazone,* m.p. $110\text{--}111^\circ$. β -C₁₀H₇ styryl ketone, m.p. 104° (syn-semicarbazone, m.p. 185°), with NHPH·NH₂ (III) at 145° gives 1:5-diphenyl-3- β -naphthylpyrazoline, m.p. $180\text{--}181^\circ$. β -C₁₀H₇ p-methoxystyryl ketone, m.p. 96° (syn-semicarbazone, m.p. 188°), with (III) at 160° gives 1-phenyl-5-p-anisyl-3- β -naphthylpyrazoline, m.p. $141\text{--}142^\circ$. β -C₁₀H₇ 3:4-methylenedioxystryryl ketone, m.p. $142\text{--}144^\circ$, gives a syn-semicarbazone, m.p. $203\text{--}204^\circ$. The compounds marked * are phototropic, as are the (*anti*) phenylhydrazones of CHPh:CH·COEt and CHPh:CH·COPr^a, but not the (*syn*) phenylhydrazones of CHPh:CH·COMe or CHPh:CH·CET·COMe. Phototropism of (I) [more stable to light than (II)] is attributed to admixed (II). E. W. W.

Pinacols and the pinacolone rearrangement.

II. E. BERGMANN (Rec. trav. chim., 1939, 58, 863—870).— α -Diphenyl- β -di-*p*-tolylethane- α - β -diol when treated successively with MgEtBr and H₂O is recovered unchanged, indicating non-dissociation of the central C·C linking (cf. Gomberg *et al.*, A., 1927, 245, 1190). The theory that the rearrangement involves an ionic compound, formation of which is favoured by the high dielectric const. of the usual acidic reagents, is not supported by the fact that PhNCO acts as a dehydrating agent [forming CO(NHPH)₂]. Fluorenepinacol thus gives diphenylenephenanthrone (also formed in boiling PhOEt), *p*-chlorobenzophenonepinacol gives impure *p*-C₆H₄Cl·CPh₂·CO·C₆H₄Cl·*p*, benzylhydroanisole gives CH₂Ph 4:4'-dimethoxybenzhydryl ketone, but benzylhydrobenzoin (I) yields its cyclic carbonate, m.p. $119\text{--}120^\circ$ [also formed from (I) and COCl₂ in PhMe-quinoline], probably by way of CH₂Ph·CPh(OH)·CHPh·CO₂·NHPH and loss of NH₂Ph. *o*-Fluorobenzophenonepinacol, m.p. $188\text{--}195^\circ$, from *o*-C₆H₄F·COPh and Zn·AcOH, is rearranged (boiling AcOH-I; not AcCl) with difficulty to *o*-fluorophenyl *o*-fluorotriphenylmethyl ketone, m.p. $132\text{--}133^\circ$, hydrolysed by MeOH-KOH to *o*-fluorotriphenylmethane (II), m.p. $85\text{--}87^\circ$. *o*-C₆H₄F·CO₂Me with PhBr and Mg yields *o*-fluoro-

triphenylcarbinol, m.p. 116° , converted by AcCl-HCl in C₆H₆ into *o*-fluorotriphenylmethyl chloride, m.p. $110\text{--}111^\circ$, which with Na-Hg in Et₂O yields (II). The difficulty of rearrangement of pinacols from *o*-C₆H₄Hal·COPh is considered to be due to electron sharing between the halogen and adjacent OH groups rather than to steric hindrance. Data on the thermal decomp. (in PhOEt at $136\cdot8^\circ/285$ mm. to $155^\circ/515$ mm.) of (CPh₂·OH)₂ and (*o*-C₆H₄R·CPh·OH)₂ (R = F, Cl, Br, Me) are given. J. D. R.

Pyrocatechol alkyl ketones.—See B., 1939, 918.

Identification of 1:2:3:4:5:6:7:8-octahydrophenanthrene. F. BERGMANN and E. BERGMANN (J.C.S., 1939, 1364).—The assumed 1:2:3:4:5:6:7:8-octahydrophenanthrene (A., 1939, II, 363) is identified by converting it and an authentic specimen into the same 9-Ac derivative, m.p. $52\text{--}53^\circ$ (semicarbazone, m.p. $201\text{--}203^\circ$), by AcCl and AlCl₃ in PhNO₂ at $0\text{--}5^\circ$. H. B.

Preparation of substituted cyclopentanones.

I. H. A. WEIDLICH and G. H. DANIELS (Ber., 1939, 72, [B], 1590—1598).—cyclopentenones (I) are obtained by the successive addition of an acylacetic ester and α -Br-ketone to powdered Na under Et₂O whereby, after heating, the undistillable ester is almost quantitatively obtained and is then hydrolysed by 2% aq. NaOH; further quantities of (I) are obtained by acidifying the alkaline filtrates. (I) is hydrogenated in EtOH containing Pd-sponge or, preferably, PdO₂. The following are described: 3-phenyl-2-methyl- Δ^2 -cyclopentenone b.p. $163^\circ/11$ mm., m.p. $47\text{--}48^\circ$ [semicarbazone, m.p. 238° (decomp.)], from COEt·CH₂·CO₂Et and COPh·CH₂Br, hydrogenated to 3-phenyl-2-methylcyclopentanone, b.p. $158^\circ/15$ mm. [semicarbazone, m.p. $209\text{--}210^\circ$ (decomp.)]; 3-phenyl-5-methyl- Δ^2 -cyclopentenone, b.p. $130^\circ/0\cdot4$ mm., m.p. 41° [semicarbazone, m.p. 211° (decomp.)], whence 3-phenyl-5-methylcyclopentanone, b.p. $110\text{--}114^\circ/0\cdot6$ mm. (semicarbazone, m.p. 162°); 5-phenyl-2:3-dimethylfuran, b.p. $110\text{--}115^\circ/0\cdot4$ mm., obtained by rapid heating of CH₂Ph·CO·CMeAc·CO₂Et with NaOH, and identified as the adduct, C₁₆H₁₄O₄, m.p. 195° , with maleic anhydride; (?) 3-bromo-2:4-diphenylfuran, m.p. 122° ; 3-phenyl-4-methyl- Δ^2 -cyclopentenone, m.p. 73° (semicarbazone, m.p. 203°), reduced to 3-phenyl-4-methylcyclopentanone, b.p. $100\text{--}104^\circ/0\cdot3$ mm. (semicarbazone, m.p. 162°). 3-Phenylcyclopentanone is transformed by successive treatments with Na in liquid NH₃ and CH₂Cl·CO₂Et into phenylcyclopentylidenephenylcyclopentanone, b.p. $184^\circ/0\cdot4$ mm., m.p. $113\text{--}114^\circ$. CHAcNa·CO₂Et and 2-C₁₀H₇·CO·CH₂Br yield Et 2-naphthacylacetoacetate, m.p. $64\text{--}65^\circ$, cyclised (dil. alkali) to a mixture of 3-hydroxy-3- β -naphthylcyclopentanone, m.p. $83\text{--}84^\circ$, and 3- β -naphthyl- Δ^2 -cyclopentenone, m.p. $126\text{--}127^\circ$ [semicarbazone, m.p. 244° (decomp.)], reduced to 3- β -naphthylcyclopentanone, b.p. $150\text{--}153^\circ/0\cdot2$ mm., m.p. 61° [semicarbazone, m.p. $196\text{--}197^\circ$; (CHPh)₂ derivative, m.p. $211\text{--}212^\circ$]. COEt·CH₂·CO₂Et and 2-C₁₀H₇·CO·CH₂Br afford Et 2-naphthacylpropionylacetate, m.p. $70\text{--}71^\circ$ (with small amounts of 2:4-diketo-3-propionyl-3:5-di- β -naphthacyl-6-ethyl-2:3-dihydropyran, m.p. $209\text{--}214^\circ$), cyclised to 3- β -naphthyl-2-methyl- Δ^2 -cyclo-

pentenone, m.p. 128—129°, which is reduced to 3- β -naphthyl-2-methylcyclopentanone, m.p. 84.5° (semicarbazone, m.p. 213—214°). An incomplete cyclisation led to *Et* 5- β -naphthyl-2-ethylfuran-3-carboxylate, m.p. 61—62° (acid, m.p. 196°).

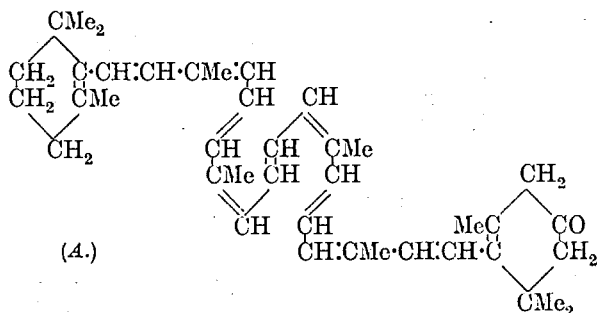
[With H. KNAUBER and F. KÜBLER.] The ester obtained from $\text{CHAcNa} \cdot \text{CO}_2\text{Et}$ and 2-bromo-1-keto-1:2:3:4-tetrahydronaphthalene is converted by distillation or boiling with HCl (1:1) into *Et* 1-methyl-3:4-dihydro-5:6-benzocoumarone-2-carboxylate, b.p. 152°/0.4 mm. (acid, m.p. 225—226°), and by NH_3 in excess of AcOH into *Et* 2-methyl-4:5-dihydro-6:7-benzoindeole-3-carboxylate, m.p. 156—157°.

H. W.

Oxidation of cyclopentenones. I. J. RINKES (Rec. trav. chim., 1939, 58, 722—724).—Oxidation of 2-*n*-hexyl- Δ^2 -cyclopentenone with KMnO_4 in COMe_2 yields $\gamma\delta$ -diketoundecoic acid, m.p. 99—100° (dioxime, m.p. 174°). Similarly, 2-*n*-butyl- Δ^2 -cyclopentenone gives $\gamma\delta$ -diketononoic acid, m.p. 96°.

J. D. R.

Carotenoids of fresh-water algæ. VII. Polyene pigments of the blue alga *Aphanizomenon flos-aquæ*. II. J. TISCHER (Z. physiol. Chem., 1939, 260, 257—271; cf. A., 1938, III, 360).—Aphanin (I) (probably A), m.p. 180° (corr.) [oxime, m.p. 208° (corr.)], spectrum very similar to that of (I)], is optically inactive. It contains 6 CMe, 11 C:C, and 1 CO but no CMe₂ and hence is not a derivative of γ -carotene. (I) in $\text{C}_6\text{H}_6 + \text{Pr}^\beta\text{OH}$ and $\text{Al}(\text{OPr}^\beta)_3$ give aphanol and other products separated by adsorption



on Al_2O_3 . Aphanicin (II), $\text{C}_{30}\text{H}_{106}\text{O}_3$, m.p. 195° (corr.) (oxime, m.p. 241°), which also contains 1 CO (not in the conjugated system) and 11 C:C, is reduced by $\text{Al}(\text{OPr}^\beta)_3 \cdot \text{Pr}^\beta\text{OH}$ to aphanicol. Possibly (II) is made up of 2 mols. of (I) (less 2 H) united by O and contains only one non-substituted β -ionone ring. Aphanizophyll (III) (possibly related to lycopene) yields an oxime (CO not in conjugated system) and a palmitate. 2.25 kg. of the dry alga contain 1.3 g. of palmitic acid, which accompanies (III). W. McC.

Synthesis of derivatives of fluorene from 1-hydrindone via the "Mannich" reaction. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 72, 284—292).—1-Hydrindone, morpholine hydrochloride, and paraformaldehyde in boiling abs. EtOH give 2-morpholinomethyl-1-hydrindone (I), b.p. 130—152°/3.5 mm. (considerable decomp.) (hydrochloride, m.p. 162°; picrate, m.p. 146°), and a by-product, $\text{C}_{24}\text{H}_{25}\text{O}_3\text{N}$, m.p. 143° (picrate, m.p. 169°). The successive action of MeI and $\text{CHAcNa} \cdot \text{CO}_2\text{Et}$ on (I) leads to *Et* 3-keto-1:2:3:10-

tetrahydrofluorene-2-carboxylate (II), m.p. 157° (dinitrophenylhydrazone, m.p. 185°; pyrazolone, $\text{C}_{20}\text{H}_{16}\text{ON}_2$, m.p. 288°). (II) is converted by boiling $\text{KOH} \cdot \text{MeOH}$ into tarry products but is hydrolysed and decarboxylated in glycerol containing 10% of H_2O at 180—190° to 3-keto-1:2:3:10-tetrahydrofluorene (III), b.p. 170—173°/2 mm., m.p. 100° (dinitrophenylhydrazone, m.p. 248°; semicarbazone, m.p. 234°). This is hydrogenated (Pd-norit) to 3-keto-1:2:3:4:10:11-hexahydrofluorene, b.p. 142—144°/1.3 mm. (dinitrophenylhydrazone, m.p. 215°; semicarbazone, m.p. 220°). Na and EtOH reduce (III) to 3-hydroxy-1:2:3:4:10:11-hexahydrofluorene (IV), b.p. 135—140°/1.2 mm., which does not give a cryst. acetate, *p*-nitrobenzoate, or phenylurethane. When heated with Pd-C at 330—335° (III) gives 3-hydroxyfluorene, m.p. 137°. Zn-Hg and boiling HCl reduce (IV) to 1:2:3:4:10:11-hexahydrofluorene, b.p. 136—138°/23 mm. Dimethoxy-1-hydrindone analogously gives 5:6-dimethoxy-2-morpholinomethyl-1-hydrindone hydrochloride, m.p. 183° (corresponding picrate, m.p. 185—186°). A "Mannich" base could not be prepared from 2-hydrindone.

H. W.

Separation and purification of ketones of the sterol series.—See B., 1939, 995.

Δ^1 -Unsaturated steroid ketones. A. BUTENANDT, L. MAMOLI, H. DANNENBERG, L. W. MASCH, and J. PALAND (Ber., 1939, 72, [B], 1617—1623).—The compounds previously designated (lit. 1935—1938) Δ^1 -cholestenone, m.p. 111—112°, Δ^1 -3-ketobisnorallocholenic acid, m.p. 235°, Δ^1 -alloprenedione, m.p. 140°, Δ^1 -androstenedione, m.p. 139—140°, and Δ^1 -androstenolone, m.p. 158—159°, and obtained by the action of KOAc in AcOH at 180—200° on the requisite 2-Br-ketones (I) do not possess the structures indicated and are provisionally termed "*hetero*- Δ^1 -ketones." The normal Δ^1 -unsaturated steroid ketones are obtained in good yield and certain structure from (I) and boiling collidine (II). Thus 2-bromocholestanone gives Δ^1 -cholestenone, m.p. 95°, $[\alpha]_D^{25} + 64.5^\circ$ in EtOH, hydrogenated (Pd-CaCO₃-MeOH) to cholestanone. 2-Bromoalloprenanedione (III) affords a pyridinium bromide, m.p. 286° (decomp.), which passes at 270—280°/14 mm. into Δ^1 -alloprenedione, m.p. 202—204°, $[\alpha]_D^{25} + 126^\circ$ in CHCl_3 [also from (III) and boiling (II)], hydrogenated (Pt in AcOH) to alloprenanedione, m.p. 200°. 2-Bromoandrostane-3:17-dione yields Δ^1 -androstene-3:17-dione, m.p. 138—139°, $[\alpha]_D^{25} + 148.5^\circ$ [dioxime, m.p. 258—264° (decomp.)], whence androstane-3:17-dione. 2:4-Dibromocholestanone gives Δ^1 : Δ^4 -cholestadienone, m.p. 108—110°, $[\alpha]_D^{25} + 31^\circ$.

H. W.

Behaviour of dehydroisoandrosterone and androsterone in the *m*-dinitrobenzene reaction. G. O. LANGSTROTH and N. B. TALBOT (J. Biol. Chem., 1939, 129, 759—768; cf. A., 1939, II, 378).—Absorption spectra (λ 3100—6500 Å.) show that androsterone and dehydroisoandrosterone give identical results.

A. T. P.

Degradation of hydoxycholeic acid to bisnorhydoxycholeic acid and pregnane-3:6-diol-20-one. T. KIMURA and G. SUGIYAMA (J. Biochem. Japan, 1939, 29, 409—419).—Me hydoxycholeate

with MgMeI gives the corresponding *dimethylcarbinol*, m.p. 215—216°, the *diacetate* (I), m.p. 110°, of which is oxidised (CrO_3) to the Ac_2 derivative (II), m.p. 140°, of *norhyodeoxycholic acid*, m.p. 209°, $[\alpha]_D^{25} +6.32^\circ$ in EtOH [*dehydro*-derivative, m.p. 211°; *Me* (+0.5 H_2O), m.p. 115°, and *Et* ester, m.p. 124°], which, similarly treated, yields the *dimethylcarbinol*, m.p. 241° [*diacetate* (III), m.p. 151°], and Ac_2 derivative of *bisnorhyodeoxycholic acid*, $\text{C}_{29}\text{H}_{46}\text{O}_5$, m.p. 238°, $[\alpha]_D^{25} -12.9^\circ$ in EtOH [*Me* ester (IV), m.p. 137°]. Partial oxidation (CrO_3) of (I) gives a *ketone diacetate*, $\text{C}_{29}\text{H}_{46}\text{O}_5 \cdot \text{H}_2\text{O}$, m.p. 163°, further oxidised to some (II) and hydrolysed to a 3:6-*dihydroxyketone*, $\text{C}_{25}\text{H}_{42}\text{O}_3 \cdot 0.5\text{H}_2\text{O}$, m.p. 183°, $[\alpha]_D^{25} +19.81^\circ$ in EtOH, whilst (III) gives a *ketone diacetate*, m.p. 178°, hydrolysed to a 3:6-*dihydroxyketone*, $\text{C}_{24}\text{H}_{40}\text{O}_3 \cdot \text{H}_2\text{O}$, m.p. 233°, $[\alpha]_D^{25} -3.17^\circ$ in EtOH. The *diethylcarbinol* (+ H_2O), m.p. 195°, from (IV) and MgEtBr , is successively acetylated, oxidised, and hydrolysed to *pregnane-3:6-diol-20-one*, m.p. 198°, $[\alpha]_D +6.52^\circ$ in EtOH.

F. O. H.

Degradation of deoxycholic acid to a *dihydroxyketone*, $\text{C}_{19}\text{H}_{32}\text{O}_3$, and 3:12-*diketo-22-methyl- Δ^{20} -norcholene*. T. KAZUNO and T. SHIMIZU (J. Biochem. Japan, 1939, 29, 421—433).—*Me* deoxycholate with MgMeI and MgEtI affords the corresponding carbinols, non-cryst. and m.p. 115°, (sinters at 85—87°) respectively, the respective *diacetate* (I), m.p. 107—110°, and *triacetate* (II), m.p. 149°, of which are oxidised (CrO_3) to *nordeoxycholic acid diacetate*, m.p. 206—207.5° (*Me* ester, m.p. 157°), hydrolysed to *nordeoxycholic acid*, m.p. 211—212°, $[\alpha]_D^{25} +57.68^\circ$ in EtOH [*Me* ester (III), m.p. 110—112°]. (III) with MgMeI yields the corresponding *dimethylcarbinol*, the *triacetate* of which is oxidised and then hydrolysed to *bisnordeoxycholic acid*, m.p. 235—237° (sinters at 200°), $[\alpha]_D^{25} +53.14^\circ$ in EtOH [*Me* ester, m.p. 167°; *dimethylcarbinol* (IV) and *diphenylcarbinol* derivative (+0.5 H_2O), m.p. 227°]; a by-product is a *ketone diacetate*, m.p. 148—150°. Oxidation (CrO_3 - AcOH) of acetylated (IV) yields 3:12-*diacetoxy-22-methyl- Δ^{20} -norcholene*, m.p. 166°, hydrolysed to the 3:12-(OH)₂-derivative, m.p. 206° (oxidised to the 3:12-*diketo*-derivative, m.p. 181—182°). Oxidation of (I) also gives a *ketone diacetate*, $\text{C}_{29}\text{H}_{46}\text{O}_5$, m.p. 141°, and (II) affords a *ketone diacetate*, $\text{C}_{23}\text{H}_{34}\text{O}_5$, m.p. 205—206°, and a *ketone triacetate*, $\text{C}_{34}\text{H}_{54}\text{O}_7$, m.p. 180°. Direct oxidation of deoxycholic acid gives a *dihydroxyketone*, $\text{C}_{19}\text{H}_{32}\text{O}_3$, oxidised to a 3:12:17-triketone. Structures of the above neutral by-products are given.

F. O. H.

Δ^{16} -*alloPregnene-3:20-dione*. A. BUTENANDT, L. MAMOLI, and A. HEUSNER (Ber., 1939, 72, [B], 1614—1617).—Androsterone acetate in EtOH is transformed by KCN and AcOH into the corresponding cyanohydrin, decomp. 192°, which with POCl_3 in $\text{C}_5\text{H}_5\text{N}$ gives the Δ^{16} -*acetoxynitrile*, m.p. 198—200°. This is transformed by MgMeBr into Δ^{16} -*epiallopregnen-3-ol-20-one*, m.p. 226°, $[\alpha]_D^{24} +54^\circ$ in CHCl_3 (acetate, m.p. 159°, $[\alpha]_D^{24} +57^\circ$ in CHCl_3), which is oxidised by CrO_3 in AcOH to Δ^{16} -*allopregnene-3:20-dione*, m.p. 205—208°, $[\alpha]_D^{24} +72^\circ$ in CHCl_3 (*dioxime*, decomp. 198—202°).

H. W.

Derivatives of pregnane- and pregnene-dione.—See B., 1939, 996.

Vitamin- K_1 , $\text{C}_{32}\text{H}_{48-50}\text{O}_2$, and $-K_2$, $\text{C}_{40}\text{H}_{54-56}\text{O}_2$. α -Phylloquinone, $\text{C}_{30}\text{H}_{44(46)}\text{O}_2$ or $\text{C}_{32}\text{H}_{48(50)}\text{O}_2$, and diacetyl- α -dihydrophylloquinone. Vitamin- K_1 dihydro-diacetate, $\text{C}_{36}\text{H}_{54-56}\text{O}_4$, m.p. 59°, and vitamin- K_2 dihydro-diacetate, $\text{C}_{44}\text{H}_{60-62}\text{O}_4$, m.p. 57—58°.—See A., 1939, III, 853.

Chemical nature of the substance secreted by the eggs of *Arbacia pustulosa* to allure the spermatozoa. R. KUHN and K. WALLENFELS (Ber., 1939, 72, [B], 1407—1413).—The ovaries are triturated with sand in the presence of aq. COMe_2 containing a little AcOH, extracted with COMe_2 -HCl, and the dark red extract + H_2O is exhaustively treated with Et_2O . The Et_2O solution yields to aq. NaHCO_3 *echinochrome A* (I), $\text{C}_{12}\text{H}_{10}\text{O}_7$, m.p. 220° (decomp.). Reductive acetylation (Zn dust and Ac_2O in presence of $\text{C}_5\text{H}_5\text{N}$) converts (I) into *dihydroechinochrome A hepta-acetate*, $\text{C}_{26}\text{H}_{26}\text{O}_{14}$, decomp. 240—245°, whilst Et_2O -EtOH- CH_2N_3 yields *trimethylechinochrome A*, m.p. 129—130° (Berl) (insol. in NaHCO_3 ; blue-violet solution in dil. NaOH). Distillation with Zn dust yields a small amount of C_{10}H_8 and oxidation with CrO_3 affords EtCO_2H . It is therefore probable that leucoechinochrome A is 1:3:4:5:6:7:8-heptahydroxy-2-ethylnaphthalene and that the pigment is the related 1:4- or 5:8-quinone.

H. W.

1:4:5:8-Tetra-aminoanthraquinone.—See B., 1939, 918.

Completely substituted anthraquinones and the corresponding anthracenes. I. Symmetrically substituted anthracenes. H. J. BACKER, J. STRATING, and L. H. H. HUISMAN (Rec. trav. chim., 1939, 58, 761—777).— γ -8-Dimethyl- Δ^{58} -hexadiene and *p*-benzoquinone (I) yield 1:2:3:4:5:6:7:8-octamethyloctahydroanthraquinone (II), m.p. 142—153°, oxidised by O_2 in EtOH-KOH to 1:2:3:4:5:6:7:8-octamethyl-1:4:5:8-tetrahydroanthraquinone, (III), m.p. 279—280°, which with N_2H_4 at 230° yields 9:10-dihydroxy-1:2:3:4:5:6:7:8-octamethyl-1:4:5:8:9:10-hexahydroanthracene (IV), m.p. 310° [oxidised by air in EtOH-KOH to (III)], together with the *quinhydrone*, m.p. 303° [prep. also from (III) and (IV)]. Oxidation of (II) with O_2 in NaOBu-BuOH yields octamethylantraquinone, m.p. 303°, reduced by red P and HI to octamethylanthrone, m.p. 251—252°, and (Clemmensen) to octamethyl-9:10-dihydroanthracene, m.p. 283—284°, which is dehydrogenated by Se in C_{10}H_8 at 230° to 1:2:3:4:5:6:7:8-octamethylantracene, m.p. 299—300° [*picrate*, decomp. $\sim 233^\circ$; $\text{C}_6\text{H}_5(\text{NO}_2)_3$ compound, decomp. $\sim 265^\circ$]. Di- Δ^1 -cyclopentenyl (2 mols.) and (I) in BuOH give 1:2:3:4:5:6:7:8-tetracyclopenteno-octahydroanthraquinone (improved yield), m.p. 146—151° (lit. 153°), which is oxidised by O_2 in NaOBu-BuOH to tetracyclopentenoanthraquinone, m.p. 362°, reduced (Clemmensen) to tetracyclopenteno-9:10-dihydroanthracene, m.p. 377—378°, which is dehydrogenated (Se) to tetracyclopentenoanthracene, decomp. $>300^\circ$. Di- Δ^1 -cyclohexenyl and (I) in C_6H_6 followed by fractional crystallisation yield three stereoisomerides

of 1:2:3:4:5:6:7:8-tetracyclohexeno-octahydro-anthraquinone, m.p. 217—217.5°, 303—304°, and 136.5—137.5°. In PhMe, another isomeride, m.p. 249—250°, is obtained. The mixture of isomerides is oxidised by O₂ in NaOBu-BuOH to 1:2:3:4:5:6:7:8-tetracyclohexenoanthraquinone, m.p. 362°, which is reduced to tetracyclohexeno-9:10-dihydroanthracene, m.p. 382—383°, dehydrogenated by Se in C₁₀H₈ at 230° to tetracyclohexenoanthracene, m.p. >380°. J. D. R.

Hypericin, the photodynamically active pigment of *Hypericum perforatum*. H. BROCKMANN, M. N. HASCHAD, K. MATER, and F. POHL (Naturwiss., 1939, 27, 550).—*Hypericin* (I), C₂₈H₁₀O₂(OH)₆, the red pigment of *H. perforatum* (St. John's wort), is isolated in cryst. form, decomp. ~330° (? hexa-acetate, decomp. when heated, and benzoate, m.p. 224—226°). (I) in solution exhibits a red fluorescence, and in EtOAc has absorption max. at 597, 554, and 516, and in C₅H₅N, 603, 559, and 520 mμ. Solutions in alkali hydroxide, conc. H₂SO₄, and Ac₂O + boroacetic anhydride exhibit a green colour. (I) is probably a hexahydroxymesodianthrone. (I) is responsible for the photodynamic activity of *H. perforatum* producing hypericisms in grazing animals. (I) injected into, or fed to, rats or mice with subsequent illumination produces the characteristic alteration of body temp. and final death.

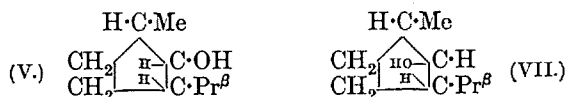
S. H. H.

Processes of polymerisation. III. Condensation of 1:4-naphthaquinone to triphthalylbenzene by pyridine. R. PUMMERER, A. PFAFF, G. RIEGELBAUER, and E. ROSENHAUER (Ber., 1939, 72, [B], 1623—1634; cf. A., 1938, II, 65; 1939, II, 78).—1:4-Naphthaquinone (I), and 1:4-C₁₀H₆(OH)₂ (II) in AcOH are converted by air into triphthalylbenzene (III) and 1:4:1':4'-tetrahydroxy-2:2'-dinaphthyl (identified as the tetra-acetate, m.p. 226°). 2:2'-Dinaphthyl-1:4:1':4'-diquinone (IV), (II), and BzOH in *o*-C₆H₄Cl₂ at 185° give the green anhydroquinhydrone of (III). In C₅H₅N, (III) results from a mixture of (IV) and (II) but appears to be derived entirely from (II) without participation of (IV). (IV), obtained in 65—70% yield by the polymerisation of (I) in EtOH containing some AcOH and quinoline, with N₂H₄.H₂O in PhNO₂ (suspension) gives a monohydrazone, decomp. ~300°. (IV) is isomerised in boiling 1-C₁₀H₇NO₂ to 4'-hydroxy-2:2'-dinaphtha-3:1'-furan-1:4'-quinone (V), decomp. >360° (sealed tube) [*o*-chlorobenzoate, m.p. 379—380° after softening at 376° if placed in bath at 250°]. Reducing acetylation of (V) affords a colourless dihydrotriacetate, m.p. 297° (corr.; decomp.) when placed in Cu block preheated to 260°. (III) is reduced by HI to trinaphthylene, a violet quinone, C₃₀H₁₄O₃, m.p. 362° (leucodiacetate, decomp. 328° in bath preheated to 310°), and a blue dihydroxyquinone, C₃₀H₁₆O₄ (diacetate). (III) and N₂H₄.H₂O in boiling C₅H₅N-PhNO₂ afford triphthalylbenzenebisdiazine, C₃₀H₁₂O₂N₄, decomp. >420°. H. W.

Camphorophorone and pulegone: hydrogenation products and their structure. I. II. Hydrogenation by sodium in presence of aqueous ether or of absolute alcohol. III. Hydrogen-

ation in presence of metallic catalysts. R. CALAS (Bull. Soc. chim., 1939, [v], 6, 1374—1382, 1382—1391, 1391—1401).—I. *Th d-camphorone* at 300—400° (vac.) gives camphorophorone (2-methyl-5-isopropylidenecyclopentanone) (I) (41% yield), with a smaller amount of pulegone (2-methyl-5-isopropyl-Δ⁴-cyclopentenone) (II), [α]_D²⁰ +0.73°, and some 2-methylcyclopentanone.

II. In aq. Et₂O, Na reduces (I) to approx. equal quantities of 1:1'-dihydroxy-2:2'-dimethyl-5:5'-diisopropylidencyclopentyl (III), m.p. 182—183° [not the diisopropylidene compound, as stated by Kerp (A., 1896, i, 447)], and a mixture, b.p. 81—82°/14 mm. This yields the *H phthalate* (IV), m.p. 114°, of cis- (V) (*p*-nitrobenzoyl derivative, m.p. 71°) and, in larger proportion, the *H phthalate* (VI), m.p. 84°, of trans-dihydrocamphorol (VII) (*p*-nitrobenzoyl derivative, m.p. 58°). (V) and (VII) are oxidised by CrO₃ to dihydro-

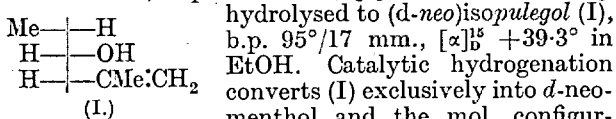


camphorophorone. The *cis*- and *trans*-structures are respectively assigned because (VI) is formed in larger quantity, and is hydrolysed much more rapidly by dil. H₂SO₄ than is (IV); also (VII) is more viscous than (V). The mol. refraction of (V) is, however, greater than that of (VII). Parachors are almost identical. Reduction of (II) similarly gives (III), (V), and (VII). With Na in anhyd. EtOH, (I) gives (VII), a smaller proportion of (V) than before, and very little (III). (II) behaves similarly.

III. With H₂ and Raney Ni in EtOH (neutral or alkaline), (I) and (II) both give a mixture of *cis*- and *trans*-dihydrocamphorophorone (semicarbazones, m.p. 209° and 198°) (cf. Godchot *et al.*, A., 1913, i, 348).

E. W. W.

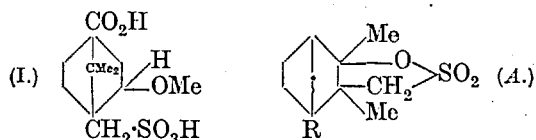
Menthone series. XVI. (*d*-neo)isopulegol. A. G. SHORT and J. H. READ (J.C.S., 1939, 1306—1309).—Reduction of *d*-pulegone by the Ponndorf reagent gives a mixture of pulegols and isopulegols, from which, after treatment with 3:5-dinitrobenzoyl chloride, can be separated (*d*-neo)isopulegyl 3:5-dinitrobenzoate, m.p. 138—139°, [α]_D¹⁹ +45.0° in CHCl₃,



hydrolysed to (*d*-neo)isopulegol (I), b.p. 95°/17 mm., [α]_D¹⁹ +39.3° in EtOH. Catalytic hydrogenation converts (I) exclusively into *d*-neomenthol and the mol. configuration is assigned. The unesterified portion from the reduction gives a ketone (2:4-dinitrophenylhydrazone, m.p. 149—150°, [α]_D¹⁹ +116.0° in CHCl₃) containing some *d*-isopulegone. F. R. S.

Action of sulphuric acid on camphenecarboxylic acids. Y. ASAHINA and H. KAWAHATA (Ber., 1939, 72, [B], 1540—1548).—In general, OH introduced by addition of H₂SO₄ at the CH₂ double linking of 1-substituted camphene derivatives immediately undergoes the Nametkin isomerisation followed by reaction with SO₃H to yield the sultone, whereas the Wagner isomerisation is preferred by 4-substituted camphene compounds. The behaviour of camphenecarboxylic acid is exceptional. *d*-Camphenecarboxylic acid is converted by conc. HCl into 2-chloro-

camphane-4-carboxylic acid, m.p. 164—165°, $[\alpha]_D^{25} +32.2^\circ$ in EtOH, transformed by boiling aq. K_2CO_3 into *2-hydroxycamphane-4-carboxylic acid*, m.p. 221—222° (decomp.), $[\alpha]_D^{25} +18.8^\circ$ in EtOAc, which is converted by boiling 0.1N- H_2SO_4 into *Dl-camphene-4-carboxylic acid*, m.p. 158—159°, $[\alpha]_D^{25} -56.5^\circ$ in EtOH. Conc. H_2SO_4 and Ac_2O convert this into *isobornyl-acetato-4-carboxylic- ω -sulphonic acid (I)* (Me_2 ester, m.p. 91°, $[\alpha]_D^{25} -3.82^\circ$ in EtOH). *Dd-Camphene-1-carboxylic acid*, conc. H_2SO_4 , and Ac_2O give *camphenhydrato-4-carboxylo- π -sulphonolactone (II)* (A ; $R = CO_2H$) [*Me* ester, m.p. 179—180°, $[\alpha]_D^{25} -16.18^\circ$ in C_6H_6 (does not react with $NH_3 \cdot MeOH$ at 100°);



Et ester, m.p. 85°]. Attempted decarboxylation of (II) by Cu-bronze at $\sim 180^\circ$ leads to *camphene-1-carboxylic acid* and by heating with H_2O at 185—195° to the optically inactive *r-camphene-4-carboxylic acid*, m.p. 131°. (II) is transformed by $SOCl_2$ into the *chloride (A)* ($R = COCl$), m.p. 199—200°, which with conc. aq. NH_3 affords the *amide (A)* ($R = CO \cdot NH_2$), m.p. 191—192°, $[\alpha]_D^{25} +10.03^\circ$ in EtOH. Addition of Br to this compound in $NaOMe \cdot MeOH$ yields the *sultonyl-4-urethane (A)* ($R = NH \cdot CO_2Me$), m.p. 136—138°, which could not be converted into the corresponding amine by dissolution in conc. H_2SO_4 or by heating with HCl. The *sultonyl-4-carbimide*, m.p. 184°, $[\alpha]_D^{25} -34.15^\circ$ in C_6H_6 , is converted by conc. H_2SO_4 at 0° into 4-aminosultone (A ; $R = NH_2$), m.p. 74—75° (*Bz* derivative, m.p. 209°). Conc. H_2SO_4 , Ac_2O , and *camphene-1-nitrile* yield the *sultone-4-nitrile (A)* ($R = CN$), m.p. 236°, $[\alpha]_D^{25} -58^\circ$ in $COMe_2$. Addition of *camphene-1-carboxylamide* to conc. $H_2SO_4 \cdot Ac_2O$ leads to *camphene-4-carboxylamide- π -sulphonic acid*, m.p. 236° (decomp.), $[\alpha]_D^{25} -65.78^\circ$ in H_2O . *Camphene-1-carboxyl chloride*, b.p. 94°/7 mm., and NaN_3 in C_6H_6 at 90—100° give *camphenyl-1-carbimide*, m.p. 234° after becoming discoloured at $\sim 200^\circ$, transformed by conc. H_2SO_4 at 0° and subsequently at room temp. into 4-aminocamphene, m.p. 130—133° (hydrochloride, decomp. $\sim 291^\circ$ after becoming discoloured at $\sim 250^\circ$, $[\alpha]_D^{25} -49.1^\circ$ in H_2O). *Dicamphenylcarbamide* has m.p. 288°. H. W.

Triterpene resinols and related acids. VIII. E. S. EWEN, F. S. SPRING, and T. VICKERSTAFF (J.C.S., 1939, 1303—1306).—Reduction of α -amyrenol (I) with $Na \cdot EtOH$ gives a compound, $C_{35}H_{56}O_3$, m.p. 231°, formed by reduction of CO: to the diol and addition of EtOH to the ethylenic linking; the compound is acetylated or benzoyleated to α -amyradienyl acetate or benzoate. Similar reduction of (I) with $Na \cdot C_5H_{11} \cdot OH$ affords a compound, $C_{35}H_{62}O_3$, m.p. 225—226°, $[\alpha]_D^{25} +41.5^\circ$ in $CHCl_3$ (cf. Ruzicka *et al.*, A., 1939, II, 330), hydrolysed (KOH) to α -amyradienol (II) and oxidised ($CrO_3 \cdot AcOH$) to α -amyrenedione. If the concn. of Na amyroxide be sufficiently great, this reduction leads to the direct formation of (II), the intermediate compound spontaneously decomp. with loss of $C_5H_{11} \cdot OH$ and H_2O . F. R. S.

Polyterpenoid compounds. I. Betulic acid from *Cornus florida*, L. A. ROBERTSON, G. SOLIMAN, and (in part) E. C. OWEN (J.C.S., 1939, 1267—1273; cf. Ruzicka *et al.*, A., 1939, II, 29).—The acid obtained from the bark has been shown to be identical with betulic acid (I) (*Na* salt). Acetylation ($Ac_2O \cdot C_5H_5N$) of (I) gives the mixed *anhydride*, m.p. 194—196°, of *O*-acetylbetulic acid and $AcOH$, which does not react with CH_2N_2 . Similarly (I) and $p\text{-NO}_2 \cdot C_6H_4 \cdot COCl$ afford a product, hydrolysed to the *p*-nitrobenzoate, m.p. $>320^\circ$, of (I). Esterification of (I) takes place only with CH_2N_2 and $C_5H_5N_2$: *Me* [*p*-nitrobenzoate, m.p. 232—233°; *p*-toluenesulphonate, m.p. 172—174° (decomp.)] and *Et* betulate, m.p. 201—202°, $[\alpha]_{D461}^{25} +11.44^\circ$ in $CHCl_3$ (acetate, m.p. 185—186°, $[\alpha]_{D461}^{25} +14.33^\circ$ in $CHCl_3$). Esterification of dihydrobetulic acid yields *Me dihydrobetulate*, m.p. 238—240°. Hydrogenation of *Et O*-acetyl- gives *Et O*-acetyl-dihydrobetulate, m.p. 205°, hydrolysed to *Et dihydrobetulate*, m.p. 208°. BzO_2H and *Me O*-acetylbetulate afford the *oxide*, m.p. 202°. $HBr \cdot AcOH$ and (I) yield a *lactone acetate*, m.p. $>350^\circ$, which is hydrolysed to a saturated *lactone (A)*, $C_{30}H_{48}O_3$, m.p. $>320^\circ$, $[\alpha]_{D461}^{25} +75.18^\circ$ in $CHCl_3$. CH_2O_2 and (I) give the *formate*, m.p. $>350^\circ$, which is hydrolysed to the *lactone (B)*, $C_{30}H_{48}O_3$, m.p. $>330^\circ$, $[\alpha]_{D461}^{25} +59.05^\circ$ in $CHCl_3$. Both lactones show a high degree of stability, and it seems probable that the ethylenic linking in (I) is in the $\beta\gamma$ - or $\gamma\delta$ -position to the $\cdot CO_2H$. *O*-Acetylbetulic acid and *Br* in $AcOH$ afford the *lactone* of *O*-acetylbromobetulic acid, m.p. 290° (decomp.), whilst with $AcOH \cdot H_2O$, the corresponding Br_2 -compound, m.p. 290—295° (decomp.), is obtained. The formation of these substances is discussed.

F. R. S.

Pigment, $C_{15}H_{10}O_6$, m.p. 273° (tetra-acetate, m.p. 187°), from *Penicillium citreo-roseum*.—See A., 1939, III, 872.

Pigments in root-bark of *Celastrus scandens*. O. GISVOLD (J. Amer. Pharm. Assoc., 1939, 28, 440—443).—The root-bark, which contains no β -carotene, yields a red, optically inactive ($CHCl_3$) pigment, *celastrol*, $C_{23}H_{36}O_3$ (?), m.p. 205° [*Ac* derivative, m.p. 241°, $[\alpha]_D^{25} -54.2^\circ$ in $CHCl_3$; *Me* ether, m.p. 217.5—218° (acetate, m.p. 132—133°)], oxidised (alkaline $KMnO_4$) to a product, m.p. 252°. The I val. indicates 3 double linkings.

F. O. H.

Vegetable tannins in Formosa. IV. Y. OSIMA (J. Agric. Chem. Soc. Japan, 1939, 15, 636—638).—*Casuarin*, m.p. 182°, $\alpha_D +19.7^\circ$ in $COMe_2 \cdot H_2O$ (1:1), $+9^\circ$ in EtOH (*hexa-acetate*, m.p. 127—128°, $\alpha_D +34.3^\circ$ in $COMe_2$, *Me* ether, m.p. 156—158°, $\alpha_D +29.2^\circ$ in $COMe_2$), a stereoisomeride of the gallo-catechin in tea leaves, has been isolated from the bark of *Casuarina equisetifolia*.

J. N. A.

Hibiscic acid, $C_6H_6O_7$.—See B., 1939, 993.

Constituents of derris root. II. T. M. MEYER and D. R. KOOLHAAS (Rec. trav. chim., 1939, 58, 875—884; cf. A., 1939, II, 176).—Hydrolysis of derride (I) with $KOH \cdot EtOH$ yields Buckley's compound (B., 1936, 1117), whilst dehydroderride, under the same conditions, gives *derridic acid*, $C_{20}H_{18}O_8$, m.p. 188°, which when oxidised with H_2O_2 gives *derric acid*,

$C_{12}H_{14}O_7$, m.p. 160°, and when oxidised with $KMnO_4$ gives rissic acid. Oxidation of (I) with CrO_3 in $AcOH$ yields a ketone ("derridenone"), $C_{20}H_{12}O_7$, m.p. 318° (hydrazone, m.p. 260—262°), and a *OH*-acid, $C_9H_6O_4$. Catalytic hydrogenation of (I) yields a substance, $C_{20}H_{26}O_5$, m.p. 161—162°, whilst with $NaOAc$ and I in $EtOH$, dehydroderride, $C_{20}H_{14}O_6$, m.p. 242.5—244°, is formed. It is suggested that (I) is the optically active precursor of Buckley's compound, and is a normal constituent of derris root, and not a degradation product of deguelin as suggested by Cahn and Boam (A., 1939, II, 33). J. D. R.

Pechmann dyes. Formation of an ester of an acid isomeric with the yellow mono-acid. P. CHOVIN (Compt. rend., 1939, 209, 169—171; cf. A., 1938, II, 333).—The mono-acid of Pechmann's dye with CH_2N_2 gives a gum whilst the di-acid gives a cryst. Me_2 ester which loses $MeOH$ to give 2-keto-5-phenyl-3- α -carboxy- β -benzoylthylidene-2 : 3-dihydrofuran (I), m.p. 165° (block), which when heated above its m.p. in vac. is converted into the yellow isomeride (II) of Pechmann's dye. Hydrolysis of (I) gives the di-acid. In solution (I) is converted into (II). Attempts to form Ac derivatives of the mono- and di-acids with keten result in cyclisation. J. L. D.

Action of mixed organomagnesium compounds on *N*-substituted 2-furoamides. N. MAXIM, I. ZUGRAVESCU, and I. FULGA (Bull. Soc. chim., 1939, [v], 6, 1339—1347).—2-Furoyl chloride and $NHPhMe$ (I), $NHPhEt$ (II), and $NHPh_2$ (III) in C_6H_6 give 2-furo-methyl- (IV), m.p. 120°, and -ethyl-anilide (V), m.p. 127°, and -diphenylamide (VI), m.p. 157°. With $MgEtBr$ or $MgBu^iBr$ in Et_2O , (IV), (V), and (VI) give 2-furyl Et ketone [semicarbazone, m.p. 172° (cf. A., 1930, 1442; Asahina *et al.*, A., 1915, i, 430; Mironesco *et al.*, A., 1935, 1503)] or Bu^i ketone, with (I), (II), and (III), respectively. With $MgPhBr$, (IV) and (VI) yield Ph 2-furyl ketone (VII) and (I) and (III), respectively, but (V) gives, as well as (II) and (VII), *N*-(2-furyldiphenylmethyl)ethylaniline, m.p. 181°. *o*- C_6H_4Me - $MgBr$ with (V) or (VI) gives *o*-tolyl 2-furyl ketone, b.p. 177°/22 mm., and (II) or (III), respectively. E. W. W.

Fixation of aromatic double bonds in hydroxy-chromones and -coumarins. Formation of azo-dyes. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 9, A, 526—530; cf. A., 1938, II, 198; 1939, II, 221).—The coupling of p - NO_2 - C_6H_4 - N_2Cl with 7-hydroxy-3-methoxy-2-methylchromone (I) and 7-hydroxyflavone in aq. $NaOH$, and with 7-hydroxy- and 7-hydroxy-4-methylcoumarin in aq. Na_2CO_3 , is described. With excess of reagent, (I) gives wholly the bis-, but the other three give chiefly the mono-, with some bis-azo dye. The coumarins readily give bis-azo dyes in $NaOH$ solution, owing to ring-opening. These results indicate no rigid fixation of the double bonds. A. LI.

Psoralen and the electro-reduction of naphthalimide. E. SPÄTH and R. HILLEL (Ber., 1939, 72, [B], 1577—1580).—Contrary to Okahara (A., 1936, 1121), ficusin (I), obtained in 2.35% yield by a modified procedure from the air-dried leaves of

Ficus carica, L., has m.p. 166—167° (corr.) and dihydroficusin has m.p. 204° (corr.). The failure of (I) to attain the m.p. of synthetic psoralen is attributed to the difficulty of the complete separation of coumarins of similar constitution. The failure of Sakurai (A., 1939, II, 388) to repeat the authors' electro-reduction of naphthalimide is possibly due to the use of unsuitable electrode material. H. W.

isoFlavones from soya bean. K. OKANO and I. BEPPU (J. Agric. Chem. Soc. Japan, 1939, 15, 645—652).—5 : 4'-Dihydroxy- ("tatoin"), m.p. 318°, and 5 : 7 : 4'-trihydroxy-3-methylisoflavone ("methylgenistein"), m.p. 298°, a glucoside of 5 : 7 : 2'-trihydroxy-8-methylisoflavone ("methylisogenistin"), m.p. 255°, and a glucoside of 5 : 7 : 2'-trihydroxyisoflavone ("isogenistin"), m.p. 265°, have been isolated from the by-product of the $EtOH$ extract of soya bean. J. N. A.

Theory of allyl isomerisation. E. SPÄTH and F. KUFFNER (Ber., 1939, 72, [B], 1580—1581).—The observation of Späth and Holzer (A., 1933, 1056) that $COMe_2$ is obtained by the ozonisation of *alloimperatorin* (I) and isohexoxic acid by the oxidation of hexahydro*alloimperatorin* shows that the $\cdot CH_2\cdot CH\cdot CMe_2$ which wanders during the isomerisation of *imperatorin* to (I) is attached by the same C to the remainder of each mol. This result precedes the similar observation of Mumm and Möller (A., 1938, II, 21). H. W.

Alkylene $\beta\delta$ -glycol formals.—See B., 1939, 915.

Aluminium chloride, new reagent for the condensation of β -ketonic esters with phenols. IV. Condensation of 4-acylresorcinols with ethyl acetoacetate. C. V. DELIWALA and N. M. SHAH (J.C.S., 1939, 1250—1253).—Respropiofenone and $CH_2Ac\cdot CO_2Et$ (I) give $(AlCl_3)$ 5-hydroxy-6-propionyl-4-methylcoumarin (II), m.p. 164—165° (*Ac* derivative, m.p. 167—168°; *oxime*, m.p. 257—258°), identical with the Fries transformation product of 5-propionoxy-4-methylcoumarin, m.p. 100—101°, prepared from the OH -compound. Acetylation (Ac_2O - $NaOAc$) of (II) yields 2' : 3' : 4-trimethylchromono-7' : 8' : 6 : 5- α -pyrone, m.p. 241—242°, and reduction (Zn - Hg - HCl) affords 5-hydroxy-4-methyl-6-propylcoumarin, m.p. 152°. A similar series of reactions with resbutyrophenone gives 5-hydroxy-6-butyryl-4-methylcoumarin, m.p. 141—142° (*Ac* derivative, m.p. 167°; *Me ether*, m.p. 83—84°; *oxime*, m.p. 210°), 5-butyroxy-4-methylcoumarin, m.p. 100—101°, 4 : 2'-dimethyl-3'-ethylchromono-7' : 8' : 6 : 5- α -pyrone, m.p. 201—202°, and 5-hydroxy-4-methyl-6-butyrcoumarin, m.p. 145—146°. 2 : 4-(OH) $_2C_6H_3\cdot CO\cdot CH_2Ph$ and (I) form 5-hydroxy-6-phenylacetyl-4-methylcoumarin, m.p. 172—173° (*Ac* derivative, m.p. 142°; *Me ether*, m.p. 78—79°; *oxime*, m.p. 257°), acetylated (Ac_2O - $NaOAc$) to 3'-phenyl-4 : 2'-dimethylchromono-7' : 8' : 6 : 5- α -pyrone, m.p. 237—238°. 4-*p*-Toluoylethylresorcinol and (I) yield 5-hydroxy-6-*p*-toluoyl-4-methylcoumarin, m.p. 204—205° (*Ac* derivative, m.p. 192—193°), acetylated to 4'-*p*-tolyl-4-methylcoumarino-7' : 8' : 6 : 5- α -pyrone, m.p. 238—239°. F. R. S.

Rottlerin. III. T. BACKHOUSE and A. ROBERTSON (J.C.S., 1939, 1257—1261).—5 : 7-Dihydroxy-

2 : 2-dimethylchroman (I) and AcCN with ZnCl_2 give 5 : 7-dihydroxy-8-acetyl-2 : 2-dimethylchroman (II), m.p. 150° (2 : 4-dinitrophenylhydrazones, m.p. $228\text{--}5^\circ$), and small amounts of the 6-Ac compound (III), m.p. 229° (2 : 4-dinitrophenylhydrazones, m.p. $227\text{--}5^\circ$); with AlCl_3 , (III) only is formed. $\text{MeI-KC}_2\text{O}_3$ and (II) afford the 7-hydroxy-5-methoxy-derivative, m.p. 78° , which condenses with EtOAc-Na to form the 8-acetoacetyl compound, cyclised to 5'-methoxy-2 : 2' : 2'-trimethylchromano-8' : 7' : 5 : 6- γ -pyrone, m.p. 168° . Condensation of (II) with PhCHO yields 5 : 7-dihydroxy-8-cinnamoyl-2 : 2-dimethylchroman, m.p. $176\text{--}177^\circ$, reduced ($\text{H}_2\text{-Pd-C}$) to the -8- β -phenylpropionyl compound (IV), m.p. 172° . $\text{CH}_2\text{Ph-CH}_2\text{-CO-CN}$ and (I) give (IV) and 5 : 7-dihydroxy-6- β -phenylpropionyl-2 : 2-dimethylchroman, m.p. 171° (oxime, m.p. $129\text{--}5^\circ$), neither of which is identical with tetrahydropicrottonone (cf. McGookin *et al.*, A., 1938, II, 199). Methylation ($\text{MeI-K}_2\text{CO}_3$) of (IV) yields 7-hydroxy-5-methoxy-8- β -phenylpropionyl-2 : 2-dimethylchroman, m.p. 104° , which is further methylated to the 5 : 7-(OMe) $_2$ -compound, m.p. 74° . Benzoylation of (IV) affords the 7-hydroxy-5-benzoyloxy-derivative, m.p. $112\text{--}113^\circ$, methylated to the 7-OMe-compound, m.p. $67\text{--}5^\circ$, which is debenzylated to 5-hydroxy-7-methoxy-8- β -phenylpropionyl-2 : 2-dimethylchroman, m.p. 158° . Oximation of 5 : 7-dimethoxy-6-formyl-2 : 2-dimethylchroman gives the oxime, m.p. 184° , dehydrated to the nitrile, m.p. $126\text{--}127^\circ$, which does not react satisfactorily with $\text{Ph}[\text{CH}_2]_2\text{MgBr}$. F. R. S.

Picrotoxin. IV. R. W. H. O'DONNELL, A. ROBERTSON, and (in part) J. C. HARLAND (J.C.S., 1939, 1261—1266).—Hydrogenation of picrotoxinin (Pd catalyst) gives a mixed product, the constituents of which appear to depend on the solvent; with Pd-C in EtOAc, a product containing β -dihydropicrotoxinin (acetate, m.p. 177°), also picrotonol (I) and dihydropicrotoxic acid, are obtained. With Pd-C in EtOH, a substance, $\text{C}_{15}\text{H}_{18}\text{O}_6$, m.p. $219\text{--}220^\circ$, is separated, together with an acid (+ H_2O), m.p. 183° (efferv.) [(OMe) $_2$ -ester, m.p. 164°]. When Pd-C is used in AcOH with a trace of HCl, the product is a mixture of α -dihydropicrotoxinin and a substance, m.p. 232° (acetate, m.p. 190°), which is the precursor of (I). As tested by hydrogenation and ozonolysis methods, α - and β -bromopicrotoxinin, α - and β -bromopicrotoxic acids, and β -picrotoxic acid do not contain a double bond. α -Picrotoxic acid contains a CMe_2 system, since on ozonolysis it yields a product which with HI-P gives a ketone, $\text{C}_{13}\text{H}_{18}\text{O}_2$, and nor- and hydroxynor-picrotic acid. F. R. S.

Cyclic sulphones formed by the addition of sulphur dioxide to butadienes. H. J. BACKER, J. STRATING, and C. M. H. KOOL (Rec. trav. chim., 1939, 58, 778—784).— CHMe:CH:CMe:CH_2 and SO_2 in Et_2O at 100° yield 2 : 4-dimethyl- Δ^3 -thiacyclopentene 1 : 1-dioxide, m.p. $39\text{--}40^\circ$ (dibromide, m.p. $121\text{--}122^\circ$). Similarly, $(\text{CHMe:CH})_2$ gives 2 : 5-dimethyl- Δ^3 -thiacyclopentene 1 : 1-dioxide, m.p. $43\text{--}43\text{--}5^\circ$. From myrcene a sulphone is similarly formed, which with Br (2 atoms) in CCl_4 yields 3-($\gamma\delta$ -dibromo- δ -methylamyl)- Δ^3 -thiacyclopentene 1 : 1-dioxide, m.p.

105° , and this with more Br (2 atoms) gives 3 : 4-dibromo-3-($\gamma\delta$ -dibromo- δ -methylamyl)thiacyclopentene 1 : 1-dioxide, m.p. 131° . $(\text{CHPh:CH})_2$ does not react with SO_2 . J. D. R.

Action of ammonia on γ -substituted α -dibromopentane. M. PLANTANIDA (J. pr. Chem., 1939, [iii], 153, 257—262).—Hydrogenation (PtO_2 in EtOH or AcOH respectively) of the requisite CH_2 derivative affords 4- α -ethylpropyl- (I), b.p. $197\text{--}198^\circ$, and 4-benzhydryl- (II), m.p. 138° , -tetrahydropyran (with a by-product, m.p. 107°). 4-*iso*Propyltetrahydropyran is transformed by 70% HBr at $100\text{--}110^\circ$ into α -dibromo- γ -isopropylpentane (I), b.p. $128\text{--}130^\circ/10\text{ mm.}$ α -Dibromo- γ - α -ethylpropyl-, b.p. $178\text{--}180^\circ/23\text{ mm.}$, $157\text{--}159^\circ/18\text{ mm.}$, and γ -benzhydryl-, m.p. 82° , -pentane are obtained analogously. 20% $\text{NH}_3\text{-MeOH}$ at $130\text{--}140^\circ$ transforms (I) into 4-isopropylpiperidine, b.p. $62\text{--}64^\circ/10\text{ mm.}$ (yield 26%) (picrate, m.p. 154° ; platinichloride, decomp. 180°), and 4 : 4'-diisopropylbispiperidinium spiran bromide, decomp. $\sim 280^\circ$. 4- α -Ethylpropylpiperidine, b.p. $71^\circ/2\text{ mm.}$ (picrate, m.p. $150\text{--}5^\circ$; platinichloride, decomp. $\sim 180^\circ$), and 4 : 4'-di-(α -ethylpropyl)bispiperidinium spiran bromide, decomp. $\sim 300^\circ$, are obtained analogously. 4-Benzhydrylpiperidine, m.p. 99° (picrate, decomp. $\sim 130^\circ$; platinichloride), and 4 : 4'-dibenzhydrylbispiperidinium spiran bromide, decomp. $>300^\circ$, are described. H. W.

Pyridinium compounds.—See B., 1939, 919.

Pyridine and quinoline derivatives. XLI. Chlorination of pyridine. J. P. WIBAUT and J. R. NICOLAÏ. XLII. Formation of (4-pyridyl)pyridinium compounds from 4-chloro- and 4-bromopyridine. J. P. WIBAUT and F. W. BROCKMAN (Rec. trav. chim., 1939, 58, 709—721, 885—894).—XLI. Interaction of Cl_2 and $\text{C}_5\text{H}_5\text{N}$ in a glass tube at $240\text{--}420^\circ$ gives 2-chloro- (I) and 2 : 6-dichloropyridine (II). At 270° , (I) is formed in good yield, with a little (II) and a pyridylpyridinium compound which gives 2- $\text{C}_5\text{H}_4\text{N-NH}_2$ (III) with NaOH. At 400° , (II) is the main product. At 200° chlorination is slow and 3 : 5-di- (IV) and 3 : 4 : 5-tri-chloropyridine (V) are formed. Chlorination of fused $\text{C}_5\text{H}_5\text{N.HCl}$ at 170° gives (IV) in good yield, with small quantities of (V) and $\text{C}_5\text{Cl}_5\text{N}$. When heated with aq. NH_3 and CuSO_4 , (I) gives (III) and (II) gives 6-chloro-2-aminopyridine.

XLII. 4-Chloropyridine (VI) (improved prep.) when kept passes into N-(4-pyridyl)-4'-chloropyridinium chloride, which with HCl yields N-(4'-pyridyl)-4-pyridone dihydrochloride; 4-bromopyridine (improved prep.) behaves in the same way as (VI).

J. D. R.

Formation of β -hydroxypyridine derivatives from hexoses and ammonium salts. I. K. ASO (J. Agric. Chem. Soc. Japan, 1939, 15, 629—633).—5-Hydroxy-2-methylpyridine, a substance probably 5 : 6-dihydroxy-2-(or -3-)methylpyridine, and a substance, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, m.p. $124\text{--}125^\circ$ (picrate, m.p. $182\text{--}183^\circ$), probably 5-hydroxy-2-hydroxymethylpyridine, have been isolated from the reaction between aq. glucose or sucrose and NH_4 salts in an autoclave.

J. N. A.

Synthesis of 2:6-dimethylpyridines substituted in position 3. A. DORNOW (Ber., 1939, 72, [B], 1548—1550).— β -Ethoxycrotonaldehyde Et_2O acetal (I) and Et aminocrotonate at 100° slowly yield Et 2:6-dimethylpyridine-3-carboxylate, b.p. $132^\circ/25$ mm., in 40% yield (picrate, m.p. 137 — 138°). Acetylacetoneimine and (I) at 100° give 3-acetyl-2:6-dimethylpyridine, b.p. $108^\circ/12$ mm. (also dihydrate, m.p. 41 — 42° , and picrate, m.p. 129 — 130°). Similarly diacetonitrile affords 3-cyano-2:6-dimethylpyridine, m.p. 83° (picrate, m.p. 179 — 180°), and benzoylacetoneimine yields 3-benzoyl-2:6-dimethylpyridine, b.p. 170 — $173^\circ/12$ mm. (perchlorate, m.p. 171 — 172°).

H. W.

Synthesis of adermin. R. KUHN, K. WESTPHAL, G. WENDT, and O. WESTPHAL (Naturwiss., 1939, 37, 469—470).—3-Methoxy-2-methylpyridine-4:5-dicarboxylic acid (cf. A., 1939, II, 177), obtained by oxidation of 4-methoxy-3-methylisoquinoline, is converted through its diamide into 4:5-dicyano-3-methoxy-2-methylpyridine, m.p. 80° , which on catalytic hydrogenation yields 3-methoxy-2-methyl-4:5-di-(aminomethyl)pyridine. When treated with HNO_2 , this base yields 3-methoxy-2-methyl-4:5-di-(hydroxymethyl)pyridine, m.p. 90° , of which the hydrochloride, m.p. 150° , is identical with adermin Me ether hydrochloride (cf. A., 1938, II, 373). When boiled with HBr this Me ether gives 3-hydroxy-2-methyl-4:5-di(bromomethyl)pyridine, converted by AgOAc into the $(\text{OH}\cdot\text{CH}_2)_2$ compound, of which the hydrochloride, m.p. 203 — 204° , is identical with adermin hydrochloride. Biological tests have confirmed the identity of the synthetic compound with the natural anti-dermatitis vitamin (cf. Möller et al., A., 1939, III, 704).

W. O. K.

Vitamin- B_6 . **Synthesis of 3-methoxy-2-methylpyridine-4:5-dicarboxylic acid.** A. ICHIBA and K. MICHII (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1939, 36, 173—177; cf. A., 1939, II, 280).—A mixture of $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NK}$ and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ at 150 — 160° gives Et α -phthalimidopropionate, m.p. 61 — 63° , which with NaOMe in boiling MeOH gives 4-hydroxy-1-keto-3-methyl-1:2-dihydroisoquinoline (I), m.p. 240° after sintering at 180° . With hot xylene (I) gives a product which with excess of POCl_3 at $120^\circ/1$ hr. is converted into 1:4-dichloro-3-methyl- and 1-chloro-4-hydroxy-3-methyl-isoquinoline, m.p. 163° , which with $\text{MeI}\cdot\text{NaOMe}$ in boiling MeOH gives 1-chloro-4-methoxy-3-methylisoquinoline (II), m.p. 49° . With $\text{Sn}\cdot\text{HCl}$ at 70 — $80^\circ/10$ hr. (II) gives 4-methoxy-3-methylisoquinoline [hydrochloride, m.p. 179 — 180° (decomp.)], which with aq. KMnO_4 at 60° gives 3-methoxy-2-methylpyridine-4:5-dicarboxylic acid, m.p. 218 — 220° (decomp.), identical with the product, $\text{C}_9\text{H}_9\text{O}_5\text{N}$, from O -methyladermin and therefore confirming the structure of vitamin- B_6 (cf. Kuhn and Wendt, A., 1939, II, 177).

J. L. D.

Constitution of the so-called "norlupinane B." V. PRELOG and R. SEIWERTH (Ber., 1939, 72, [B], 1638—1642).— Et δ -ethoxyvalerate is reduced by Na and abs. EtOH to ϵ -ethoxyamyl alcohol, b.p. $90^\circ/9$ mm., converted by PBr_3 and $\text{C}_5\text{H}_5\text{N}$ into ϵ -ethoxyamyl bromide, m.p. $85^\circ/14$ mm. This is transformed by $\text{OEt}\cdot[\text{CH}_2]_3\cdot\text{CNa}(\text{CO}_2\text{Et})_2$ into Et_2 γ -ethoxypropyl- ϵ -

ethoxyamylmalonate, b.p. 207 — $210^\circ/14$ mm. The corresponding acid is decarboxylated at 180° to α -diethoxynonane-8-carboxylic acid, b.p. 162 — $163^\circ/0.03$ mm., which is transformed by NaN_3 and conc. H_2SO_4 into δ -amino- α -diethoxynonane, b.p. 160 — $161^\circ/17$ mm. The hydrobromide is converted by successive treatment with 69% HBr at 100° and 0.1N- NaOH at 50° into 1-azadicyclo-[0, 3, 5]-decane, $\text{CH}_2<\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2>\text{CH}_2$, b.p. $80^\circ/14$ mm.

[picrate, m.p. 213 — 214° (corr.); picrolonate, m.p. 191.5° (corr.); methiodide (I), m.p. 282.5 — 283° (corr.)], identical with norlupinane B (Clemo et al., A., 1931, 499). (I) is transformed by treatment with Ag_2O , followed by distillation and hydrogenation, into 1-methylazacyclodecane, m.p. 89 — $90^\circ/20$ mm.

H. W.

Action of mixed organo-magnesium compounds on the phenylhydrazones of cyclanones. P. GRAMMATICAKIS (Compt. rend., 1939, 209, 317—319; cf. A., 1937, II, 287; 1938, II, 283).—cyclo-Hexanonephenylhydrazone with MgPhBr in Et_2O affords 1:2:3:4-tetrahydrocarbazole and 1-phenylhydrazino-1-phenylcyclohexane, m.p. 113° [hydrochloride, m.p. 215° (decomp.); oxalate, m.p. 186° ; phenylcarbamyl derivative, m.p. 172°], converted by O_2 in Et_2O or EtOH into 1-benzeneazo-1-phenylcyclohexane, m.p. 60° . Similarly 2-methylcyclohexanonephenylhydrazone (I) with MgPhBr gives 1- (II) and 5-methyl-1:2:3:4-tetrahydrocarbazole (III), and 2-phenyl-2:3-tetramethylene-3- or -1'-methyl-2:3-dihydroindole, m.p. 102° [hydrochloride, m.p. 258° (decomp.); oxalate, m.p. 166° ; Ac, m.p. 93° , and phenylcarbamyl derivative, m.p. 168°]. 3-Methylcyclohexanonephenylhydrazone with MgEtBr , MgPhBr , or $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ gives 2-methyl-1:2:3:4-tetrahydrocarbazole and other condensation products. (I) with MgMeI gives (II) and (III). cyclopentanonephenylhydrazone with MgPhBr gives, besides other substances, 2:3-trimethyleneindole, m.p. 109° , b.p. 160 — $162^\circ/<1$ mm. Some unchanged phenylhydrazone, NH_2Ph , $\text{NPh}\cdot\text{NH}_2$, and cyclanone are always obtained.

J. L. D.

Homogeneous catalytic hydrogenation.—See A., 1939, I, 529.

Quinoline derivatives.—See B., 1939, 996.

Fate in the animal body of N-substituted amino-acids. III. Fate of ON-dimethyltyrosine in the rabbit and dog. T. Tō (Z. physiol. Chem., 1939, 260, 175—180; cf. A., 1939, III, 296).—Methylhydantoin hydrochloride and anisaldehyde heated at 105 — 120° for 4 hr. with NaOAc and Ac_2O give 85.5% of 4-anisylidene-3-methylhydantoin, decomp. 225° , which is reduced by $\text{Na}\cdot\text{Hg}$ in 0.5N- NaOH to 90% of ON-dimethyltyrosinylhydantoin, decomp. 149 — 150° ; this is hydrolysed in 12 hr. by boiling aq. $\text{Ba}(\text{OH})_2$ to 75% of dl-ON-dimethyltyrosine (I), decomp. 235° . Creatinine, anisaldehyde, NaOAc , and Ac_2O heated at 130 — 140° for 90 min. give 91% of anisylidenecreatinine, decomp. 195 — 200° , which in 0.5N- NaOH is reduced by $\text{Na}\cdot\text{Hg}$ to ~86% of dihydroanisylidenecreatinine, decomp. 258° ; this also is hydrolysed to 80% of (I) by boiling aq. $\text{Ba}(\text{OH})_2$. After subcutaneous injection of the Na salt of (I) into

rabbits the urine contains the *d*-form, m.p. 240°, $[\alpha]_D^{20} +21.87^\circ$, of the acid, together with smaller amounts of unchanged *dl*-acid and of *p*-methoxyphenylpyruvic acid probably derived from the *l*-acid. When dogs are used in place of rabbits unchanged material only is found in the urine. W. McC.

Structure of murexides and alloxantines. N. M. WINSLOW (J. Amer. Chem. Soc., 1939, 61, 2089—2092).—1- (I) and 1'-phenylmurexide (II) exist as different individuals, which does not accord with resonance colour theories. $\text{CH}_2(\text{CO}_2\text{H})_2$, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}_2$, and Ac_2O in boiling CHCl_3 give 1-phenylbarbituric acid (III) (40%), malonyldi(phenylcarbamide) [hydrolysed by hot 0.6*M*- Na_2CO_3 to $\text{NHPh}\cdot\text{CO}\cdot\text{NH}_2$ and (III)], and some $\text{NHPh}\cdot\text{CO}\cdot\text{NHAc}$. Conversion of (III) into Na phenylviolurate by aq. NaNO_2 at 50°, followed by reduction by $\text{H}_2\text{S}\cdot\text{HCl}$ at 45°, gives 1-phenyluramil (IV), which with HNO_3 (*d* 1.42) at 0° gives 60—90% of 1-phenylalloxan (V). Alloxan hydrate (VI) and (IV) in H_2O at 50° give 1-phenylalloxantine, hydrolysed by hot, aq. NaOAc to Na 1-phenyldialurate (74.5%) or slowly by KOAc to K dialurate (VII). Dialuric acid [prep. *in situ* from (VI) by H_2S at 98°] and (V) in H_2O give 1'-phenylalloxantine (VIII), hydrolysed at once by KOAc to (VII) (~67%). In hot 20% aq. $(\text{NH}_4)_2\text{CO}_3$, (VI) and (IV) give (I), hydrolysed by approx. *m*-HCl to 1-phenyluramil and (VI) (determined by reduction to alloxantine). A similar method did not give (II), which, however, was obtained from (VIII) by NH_3 in dry C_6H_6 at 50° and is hydrolysed by *m*-HCl to uramil, the (V) also formed being decomposed. R. S. C.

Pyrazolones.—See A., 1939, 996.

Salts of thiolbenziminazole.—See A., 1939, I, 532.

Derivatives of 1-hydroxy-1 : 2 : 3-benzotriazole. B. Vis (Rec. trav. chim., 1939, 58, 847—855).—Interaction of N_2H_4 and 1 : 3 : 4 : 5- $\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)_2$ (I) in EtOH yields the hydrazine salt, m.p. indef. (loses N_2H_4), of 4 : 6-dichloro-1-hydroxy-1 : 2 : 3-benzotriazole (II), m.p. 193°. Similarly from 1 : 3 : 4 : 5- $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_2$ (III) is produced the N_2H_4 salt, m.p. 222° after losing N_2H_4 , of 4 : 6-dibromo-1-hydroxy-1 : 2 : 3-benzotriazole (IV), m.p. 222°. With $\text{NHMe}\cdot\text{NH}_2$ (V), (I) gives 4 : 6-dichloro-3-methyl-1 : 2 : 3-benzotriazole 1-oxide, m.p. 141°, the structure of which is confirmed by a depression of m.p. when mixed with the isomeric 4 : 6-dichloro-1-methoxy-1 : 2 : 3-benzotriazole, m.p. 110—140°, which is formed from the Ag salt of (II) with MeI. From (III) and (V) in EtOH is formed 4 : 6-dibromo-3-methyl-1 : 2 : 3-benzotriazole 1-oxide, m.p. 189°, not identical with 4 : 6-dibromo-1-methoxy-1 : 2 : 3-benzotriazole, m.p. 120°, formed from the Ag salt of (IV) and MeI. Interaction of 4 : 2 : 6 : 1- $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\cdot\text{OMe}$ (VI) and N_2H_4 in EtOH yields the N_2H_4 salt, m.p. 190°, of 6-chloro-4-nitro-1-hydroxy-1 : 2 : 3-benzotriazole, m.p. 190°, whilst with $\text{NHMe}\cdot\text{NH}_2$ (VI) gives 6 : 6'-dichloro-3 : 3'-dimethyl-1 : 2 : 3 : 1' : 2' : 3'-azoxydibenzotriazole 1 : 1'-dioxide, m.p. 194°. J. D. R.

Catalytic properties of phthalocyanines in oxidations. C. PAQUOT (Compt. rend., 1939, 209,

171—173).—When O_2 is bubbled through a suspension of Fe, Co (I), or Ni (II) phthalocyanine (0.25—0.5%) in α -pinene (III) at 50—100°/8—40 hr., verbenone (10—25%), active pineol hydrate (1—3%), and unchanged (III) (40—70%) are formed. With (I) at 100°, verbenone (2—7%), verbenol (2%), and a viscous residue (10—35%) of condensation products of (III) result. (I) is considerably inactivated after being used once, but the other two catalysts can be used repeatedly. cycloHexene containing (II) (0.4%) with O_2 at 65°/60 hr. gives Δ^2 -cyclohexenone (17%), Δ^2 -cyclohexenol (6%), $\Delta^{1:3}$ -cyclohexadiene (2%), 1 : 2-oxidocyclohexane (2%), and *cis*-cyclohexane-1 : 2-diol (4%). J. L. D.

Indoles. IX. Reaction of phenylhydrazine with "Mannich" bases. (Miss) R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 73, 14—21).—With $\text{NHPh}\cdot\text{NH}_2$ (I), 2-morpholinomethylcyclohexanone gives its phenylhydrazone, m.p. 112°, which with dry HCl in cold EtOH gives the hydrochloride, m.p. 211°, of 11-morpholinomethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine, m.p. 112° (picrate, m.p. 193°). The product from 2-piperidinomethylcyclohexanone and (I) with EtOH-HCl followed by alkali gives 11-piperidinomethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine, m.p. 95° (picrate, m.p. 207°). 11-Diethylaminomethyl- (picrate, m.p. 158°), and 11-dimethylaminomethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (picrate, m.p. 175°) are obtained similarly. With (I), 2-morpholinomethylcyclopentanone gives its phenylhydrazone, m.p. 103° (picrate, m.p. 160°), which with EtOH-HCl gives the hydrochloride, m.p. 241°, of 3-morpholinomethyl-2 : 3-trimethyleindolenine, m.p. 103° (picrate, m.p. 194°). COEt_2 , $(\text{CH}_2\text{O})_3$, and morpholine hydrochloride (100°; 5 hr.) give the hydrochloride, m.p. 131°, of β -morpholinomethylpentan- γ -one, b.p. 95—100°/2 mm. (picrate, m.p. 132°), of which the reaction product with (I) gives with EtOH-HCl an uncrystallisable product. E. W. W.

Morpholinomethyl alkyl ethers. (Miss) R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 73, 22—28).—Morpholine (I), 40% CH_2O (II), and K_2CO_3 give dimorpholinomethane, b.p. 139—140°/29 mm. By the method of McLeod and Robinson (J.C.S., 1921, 119, 1472), (I), (II), and the appropriate alcohol give the following ethers: morpholinomethyl Pr^i , b.p. 185—195°, Bu^i , b.p. 218—222°/760 mm., cyclohexyl, b.p. 140—150°/30 mm. (impure), and β -phenylethyl ether, b.p. 184°/25 mm.; di(morpholinomethyl) $\alpha\beta$ -dimethylene, b.p. 205—209°/26 mm., and $\alpha\gamma$ -trimethylene diether, b.p. 218—221°/27 mm. The following cetyl ethers were also prepared for possible use as emulsifiers: morpholinomethyl, b.p. 198—202°/1 mm. (of which the methiodide, m.p. 160°, and the methosulphate have emulsifying properties but are not sufficiently stable to be of val.); piperidinomethyl, b.p. 200—202°/1.5 mm. (methiodide, m.p. 124°), diethylaminomethyl, b.p. 183—185°/1.7 mm. (methiodide, m.p. 105°), and hexahydronicotinyl cetyl ether, b.p. 250—255°/2 mm. (gummy unstable methiodide and picrate). E. W. W.

Ammines with thiolbenzthiazole. G. SPACU and C. G. MACAROVICI (Bull. Acad. Sci.

Roumaine, 1939, 21, 173—187).—The following compounds ($X = C_7H_4NS_2$) derived from thiolbenzthiazole are described: $X_4Sn, 4H_2O$; X_4Sn ; $X_2[Ni(NH_3)_2]$; $X_2[Zn(NH_3)_2]$; $X_2[Co(C_5H_5N)_2]$; $X_2[Ni(C_5H_5N)_2]$; $X_2[Cd(C_5H_5N)_2]$; $X_2[Zn(C_5H_5N)_2]$; $X_2[Co(NH_2Ph)_2, H_2O]$; $X_2[Ni(NH_2Ph)_2, H_2O]$; $X_2[Cd en]$; $X_2[Zn en]$; $X_2[Co en_2Cl(H_2O)]$; $X[Co en_2(SCN)_2]$; $X_3[Co en_2(NH_3)_2]$; $X_6[Co((HO)_2Co en_2)_3, 4H_2O]$; $X_3[Cr en_3]$; $X_2[Ni en_3]$; $X_2[Cu en_2]$; $X_3[Co en_3, H_2O]$; $X_3[Co(NH_3)_6, 3H_2O]$.
F. J. G.

Cyanine dyes.—See B., 1939, 920.

Synthesis of 5-substituted rubans. G. R. CLEMO and E. HOGGARTH (J.C.S., 1939, 1241—1244).—3-Ketoquinuclidine (I) and PhCHO give (trace $C_5H_{11}N$) 2-benzylidene-3-ketoquinuclidine, m.p. 133° (phenylhydrazone, m.p. 184°). Quinoline-4-aldehyde [improved prep.; picrate (+EtOH), m.p. 179°] and (I) afford (HCl or piperidine acetate) 5-keto-6:9-rubanene (II), m.p. 153° (picrate, m.p. 209°; platini-chloride, decomp. >260°), which is hydrogenated (MeOH-Pd-C) to 5-ketoruban, m.p. 125—126° (phenylhydrazone, m.p. 198°; picrate, m.p. 168°). This compound is reduced [$Pr^B OH-Al(OPr^B)_3$] to ruban-5-ol, m.p. 198° (picrate, m.p. 188—189°), and with MgEtI gives 5-ethylruban-5-ol, m.p. 139° (picrate, m.p. 161°). MgEtI and (II) yield a compound, $C_{19}H_{22}ON_2$, m.p. 164° (picrate, m.p. 150°). F. R. S.

Modified cinchona alkaloids. VII. Constitution of niquidine. E. M. GIBBS and T. A. HENRY (J.C.S., 1939, 1294—1299; cf. A., 1939, II, 187).—Oxidation (ice-cold $KMnO_4$) of "niquidine" gives MeCHO, quinic acid (I), and small quantities of a substance E, $C_{17}H_{14}O_4N_2$, m.p. >300° (Me ester, m.p. 168°), and a substance F, $C_{17}H_{20}O_4N_2$, m.p. 247° (decomp.); it is suggested that E is converted into F by oxidation of $C_5H_{11}N$ to C_5H_5N . Dihydronequidine is oxidised (H_2O_2) to (I), its amine oxide, m.p. 268° (decomp.), and β -propylglutaric acid, m.p. 50° (diamide, m.p. 195°; dianilide, m.p. 219°), identical with the synthetic acid. Similar oxidation (H_2O_2) of dihydroquinidine gives (I) and its amine oxide and ω -ethylmethanetriacetic acid, m.p. 120°, $[\alpha]_D -1.3^\circ$ in H_2O [di-, m.p. 222°, and tri-anilide, m.p. 280° (decomp.)], also obtained by the hydrolysis of the CN-ester prepared from $CN \cdot CHEt \cdot CO_2Et$ and Et glutamate. These experiments confirm the constitutions previously assigned.
F. R. S.

[**Strychnine and brucine. Re-examination of the action of bromine on diketonucidine and its bearing on the structure of the alkaloids.**] H. LEUCHS (Ber., 1939, 72, [B], 1588—1589).—A reply to Holmes and Robinson (A., 1939, II, 290).
H. W.

Strychnos alkaloids. CVII. Transformation of the nitroquinones from ψ -brucine and dihydro- ψ -brucine. H. LEUCHS and H. L. LOUIS (Ber., 1939, 72, [B], 1483—1487).—The dark red isomeride (I) of the nitroquinone from ψ -brucine is unchanged by H_2SO_3 at 100° and converted into a dark red resin at 130—140°; it does not react with NH_2OH and does not afford well-defined products with CH_2N_2 . Catalytic reduction followed by crystallisation of the product from $COMe_2$ gives the product,

$C_{24}H_{29}O_6N_3, HClO_4$, blackens at 220—290°, which is the $COMe_2$ derivative of an NH_2 -phenol $C_{21}H_{25}O_6N_3, HClO_4$. Reduction of (I) with Sn and 12N-HCl gives the substance, $C_{21}H_{23}O_6N_3, HCl, 0.5H_2O$, whereby it appears that NO_2 is reduced but C:C is left untouched. Zn dust and Ac_2O transform (I) into the substance, $C_{27}H_{29}O_6N_3, HClO_4$ (Ac_3 derivative of $C_{21}H_{23}O_6N_3$). Catalytic hydrogenation of ψ -brucine in 50% AcOH continues after the consumption of 3 H and the product contains dihydrobrucine (perchlorate). Interruption at a suitable point permits the isolation of dihydro- ψ -brucine, converted by successive treatments with 5N- HNO_3 and H_2SO_3 into the quinol (perchlorate, $C_{21}H_{24}O_5N_2, HClO_4$). This is oxidised by HNO_3 to the nitroquinone hydrate (II) [perchlorate (III), $C_{21}H_{23}O_8N_3, HClO_4$]; the corresponding oxime hydrochloride and semicarbazone perchlorate are described. (II) is reduced by H_2SO_3 to the nitroquinol (perchlorate, $C_{21}H_{25}O_8N_3, HClO_4$). H_2O at 80° converts (III) into the dark red amorphous compound, $C_{21}H_{23}O_8N_3$, the perchlorate of which is hydrogenated and converted by $COMe_2$ into the perchlorate, $C_{24}H_{29}O_6N_3, HClO_4$.
H. W.

Amino-morphides and -codides. L. SMALL and F. S. PALMER (J. Amer. Chem. Soc., 1939, 61, 2186—2190).—Interaction of 6- or 8-halogeno-derivatives of morphine or codeine with bases involves in each case an allylic shift. Structures are assigned by behaviour on catalytic hydrogenation. The basic substituents reduce the physiological (especially the analgesic) action. 8-Diethylaminomorphide, m.p. 201—204° (vac.) (lit., 203°), $[\alpha]_D^{25} +49.1^\circ$ in MeOH [dihydriodide, $+1.5H_2O$, m.p. 87—93° (vac.), $[\alpha]_D^{25} +2.6^\circ$ in H_2O ; diperchlorate, m.p. 114—116° (vac.), $[\alpha]_D^{19} +4.4^\circ$ in H_2O], is described. 8-Piperidinomorphide (I) (prepared from α -chloromorphine and piperidine at 100°), m.p. 222—224° (vac.), $[\alpha]_D^{25} +28.7^\circ$ in MeOH [dihydriodide, m.p. 208—214° (vac.), $[\alpha]_D^{25} +14.9^\circ$ in H_2O ; methiodide, m.p. 243—245° (vac.), $[\alpha]_D^{25} +23.7^\circ$ in 50% (vol.) EtOH], is hydrogenated (PtO₂ in this and other cases) in 5% AcOH to phenolic 8-piperidinotetrahydro-morphide, m.p. 270—280° (vac.; decomp.), $[\alpha]_D^{25} +45.1^\circ$ in 10% AcOH (green $FeCl_3$ colour) (acetate, m.p. 172—178°). 8-Diethylaminocodide, m.p. 101—103° (lit., 102°), $[\alpha]_D^{25} +42.6^\circ$ in MeOH (diperchlorate, m.p. 180.5—183°, $[\alpha]_D^{19} +3.3^\circ$ in H_2O ; dihydriodide, m.p. 179—182°, $[\alpha]_D^{25} +22.9^\circ$ in abs. EtOH), is hydrogenated in EtOH to 8-diethylaminotetrahydro-codide, m.p. 154—157°, $[\alpha]_D^{25} +31.5^\circ$ in MeOH, or (? $+xH_2O$), m.p. 116—119° (gas) [perchlorate, m.p. 234—238° (vac.), $[\alpha]_D^{25} +18.3^\circ$ in H_2O]. Hydrogenation of 8-piperidinocodide [obtained from (I) and CH_2N_2 or from α -chlorocodide (II)], m.p. 116—117° (lit., 118°), $[\alpha]_D^{25} +25.8^\circ$ in MeOH [H_2 disulphate, m.p. 161—163.5° (vac.), $[\alpha]_D^{25} +19.8^\circ$ in H_2O ; mono-, m.p. 234—237° (vac.), $[\alpha]_D^{24} +13.3^\circ$ in H_2O], and impure di-hydriodide; methiodide, $[\alpha]_D^{25} +22.0^\circ$ in H_2O ; diperchlorate, m.p. 181—183°, $[\alpha]_D^{25} +13.2^\circ$ in 50% (vol.) EtOH], in EtOH gives the phenolic H_4 -derivative, m.p. ~125°, $[\alpha]_D^{25} +36.7^\circ$ in MeOH (green $FeCl_3$ colour), but that of the hydrochloride in AcOH gives mostly the non-phenolic H_2 -derivative, m.p. 167—169°, $[\alpha]_D^{25} -1.2^\circ$ in MeOH. Liquid NH_3 and (II) at 50° give 8-aminocodide, m.p. 128.5—129°, $[\alpha]_D^{25}$

—79.2° in EtOH [*dihydrochloride*, m.p. 300—305° (vac.; corr.), $[\alpha]_D^{24}$ —40.7° in H₂O; Ac₂ derivative, +xEtOAc, m.p. 218—220° or, in vac., 165—175°, solidifies, remelts at 205°, $[\alpha]_D^{24}$ —83.1° in EtOH], which by hydrogenation in MeOH gives the phenolic H₄-derivative, m.p. 138.5—140°, $[\alpha]_D^{24}$ —9.7° in EtOH (green FeCl₃ colour; *dihydrochloride*, $[\alpha]_D^{24}$ +6.6° in H₂O), or, as dihydrochloride in AcOH, the H₂-derivative, a glass, $[\alpha]_D^{24}$ —28.7° in EtOH [*dihydrochloride*, +H₂O, m.p. 274—277° (vac.), $[\alpha]_D^{24}$ —14.7° in H₂O]. Bromomorphide (III) and piperidine at 100° give 6-piperidinomorphide (IV), m.p. 216—217° (vac.), $[\alpha]_D^{23}$ —234.8° in MeOH [*methiodide*, m.p. 236—241° (vac.; corr.), $[\alpha]_D^{23}$ —145.8° in 50% (vol.) EtOH], which is hydrogenated in EtOH to the H₂-derivative (V), m.p. 215—217°, $[\alpha]_D^{23}$ —155.9° in MeOH. 6-Piperidinocodide, m.p. 75—80°, $[\alpha]_D^{23}$ —233.9° in MeOH (*diperchlorate*, m.p. 172—175°, $[\alpha]_D^{23}$ —113.4° in H₂O), is obtained by piperidine from (III) at 100° or β-chlorocodide at 130° or by CH₂N₂ from (IV); when hydrogenated, it absorbed 2 H to give an oil; CH₂N₂ and (V) also give an oil. Liquid NH₃ and (III) at 50° give a mixture. The bases sublime in a high vac.

R. S. C.

Veratrine alkaloids. VI. Oxidation of cevine. L. C. CRAIG and W. A. JACOBS (J. Amer. Chem. Soc., 1939, 61, 2252—2253; cf. A., 1938, II, 515; 1939, II, 459).—CrO₃ in dil. H₂SO₄ oxidises cevine to a mixture, including acids, which at 180° give CO₂ and a lactonic acid (I), C₁₄H₁₄O₆, m.p. 273—278° [$\alpha]_D^{25}$ +47.6° in C₅H₅N (reddish-purple FeCl₃ colour). CH₂N₂ gives a product (II), C₁₄H₁₂O₄(OMe)₂, m.p. 165—166°. (I) neutralises 2 NaOH—EtOH in the cold; (II) neutralises 1 NaOH—EtOH in the cold and a second mol. when boiled. p-SO₃H·C₆H₄·N₂Cl couples with (I) or (II). (I) absorbs 3 H₂ (PtO₂) to give an oil (III), which does not give the colour reactions and may be a tetrahydronaphthalene derivative; however, as, with acid, (III) liberates CO₂ (to give cryst. products), (I) may be a ketone. (I) is derived from that part of the mol. not related to octahydropyridocoline.

R. S. C.

Sulphophenylarsinic acids and their derivatives. II. p-Sulphonamidophenylarsinic acid. J. F. ONETO and E. L. WAY (J. Amer. Chem. Soc., 1939, 61, 2105—2106; cf. A., 1938, II, 464).—p-Sulphonamidophenylarsinic acid (I) (Ag salt; "anhydride" formed at 185—190°/vac.) is obtained from p-NH₂·C₆H₄·SO₂·NH₂ by the Bart reaction and from p-sulphonamidophenylarsine oxide (II) by 30% H₂O₂ at 100°. With HI, (I) gives p-sulphonamidophenyldiiodoarsine, m.p. 192—193°, with HBr·SO₂ and a trace of HI gives p-sulphonamidophenyldibromoarsine (III), m.p. 191—192°, and with HCl·SO₂ and a trace of HI or with PCl₃ gives p-sulphonamidophenyldichloroarsine, m.p. 176—177°, also obtained from (II) by hot HCl. p-SO₃Na·C₆H₄·AsO₃H₂ with PCl₅—PCl₃ gives p-chlorosulphonylphenyldichloroarsine, m.p. 84—85°, which with conc., aq. NH₃ gives (II) [also obtained from (III) by hot, aq. NH₃] and with Cl₂—CHCl₃ gives p-chlorosulphonylphenylarsinic acid (sulphonanilido-acid obtained by NH₂Ph at 100°).

R. S. C.

Arsinic acids.—See B., 1939, 997.

Preparation of p-tolylstibinic acid. G. J. BURROWS and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1939, 72, 118—119).—A diazotised solution of p-C₆H₄Me·NH₂ is added slowly and with good stirring at 0° to a solution of Na₃SbO₃ obtained by mixing SbCl₃ in conc. HCl and glycerol with aq. NaOH; excessive frothing is prevented by occasional addition of Et₂O. After keeping overnight, the mixture is filtered from coloured by-products, nearly neutralised with dil. HCl, and treated with CO₂ until Sb₂O₃ is no longer pptd.; this is filtered off and the filtrate is treated with HCl, whereby p-tolylstibinic acid is pptd. in 45—50% yield.

H. W.

Device for avoiding sucking back with the Parnas-Wagner micro-Kjeldahl apparatus.—See A., 1939, I, 540.

Micro-method for potentiometric formaldehyde titration. A. JANKE and E. MIKSCHIK (Mikrochem., 1939, 27, 176—179).—A thin glass bulb, coated externally with Ag and mounted in insulating and protective material, serves as a glass electrode and as titration vessel. A 0.01N-HCl-quinhydrone electrode is used as reference. The glass electrode vessel is placed in the axis of a loud-speaker magnet to ensure agitation of the solution. For determination of NH₂ in NH₂-acids and peptides 0.1—0.3 c.c. of the sample is introduced into the electrode and titrated with NaOH to p_H 7. 0.1—0.3 c.c. of CH₂O is then added and the solution further titrated to p_H 9. The wt. of N present is deduced from the vol. of NaOH required for the titration between p_H 7 and 9, after correction ascertained by a blank test with the same CH₂O.

J. W. S.

Oxidation of aldoses by hypiodite. III. K. MYRBÄCK (Svensk Kem. Tidskr., 1939, 51, 149—158; cf. A., 1939, II, 244).—The rate of oxidation of glucose and maltose with I in KI in presence of alkali is high in 0.031N-NaOH and in N-Na₂CO₃, but low in more conc. NaOH or in presence of NaHCO₃. In conc. NaOH the results obtained after long keeping are high owing to further stages of oxidation, whilst in Na₂CO₃ oxidation is incomplete owing to formation of IO₃⁻. The reaction becomes more complete in very dil. sugar solutions. For accurate determinations the method of Willstätter and Schudel must be followed closely.

J. W. S.

Methionine. III. Comparison of oxidative reactions of methionine, cysteine, and cystine. Determination of methionine by hydrogen peroxide oxidation. G. TOENNIES and T. P. CALLAN (J. Biol. Chem., 1939, 129, 481—490; cf. A., 1939, II, 302).—Methionine (I) is much more reactive towards H₂O₂ than cystine (II) or cysteine (III), and it may be possible to use this factor to determine (I) among the products of protein hydrolysis. Oxidation of (I) is limited to the sulphoxide stage, except in presence of MoO₄⁻, when it proceeds further; Cu⁺⁺ has no effect. Oxidation velocity of (I) or (II) increases with increasing acidity, whilst that of (III) decreases. Oxidation of (III) is also influenced by Cu⁺⁺.

A. T. P.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1939.

Electric moments in some homologous series.—See A., 1939, I, 511.

Free radicals and their importance in chemical reactions. E. OLIVERI-MANDALÀ (Chim. e l'Ind., 1939, 21, 342—345).—A lecture. O. J. W.

Reaction between methyl radicals.—See A., 1939, I, 568.

Activation of hydrogen in catalytic reactions of hydrocarbons.—See A., 1939, I, 529.

Production of ethane, quinhedrone, and potassium cupric cyanide by a.c. electrolysis.—See A., 1939, I, 530.

Kinetics of thermal decomposition of tetramethylmethane.—See A., 1939, I, 526.

Aromatisation of *n*-octane and *n*-decane in the presence of nickel-alumina catalyst. V. I. KOMAREWSKY and C. H. RIESZ (J. Amer. Chem. Soc., 1939, 61, 2524—2525).—When passed over Ni-Al₂O₃ in N₂ at 300°, *n*-C₈H₁₈ gives CH₄, H₂, and PhMe (10%, formed by way of PhEt). *n*-C₁₀H₂₂ at 350° gives CH₄, H₂, PhMe (2%), and isoparaffins (1.6%). *iso*-C₈H₁₈ and diisomyl at 300—350° give olefines, but no aromatic compounds. R. S. C.

Reactions of olefines with solid cuprous halides.—See A., 1939, I, 531.

Preparation of acetylene in the interrupted discharge.—See A., 1939, I, 573.

Radiochemical polymerisation of acetylene.—See A., 1939, I, 574.

Reactions in concentrated sulphuric acid. XV. Relationships in the case of acetylene. J. MILBAUER and Z. MILBAUER (Chem. Obzor, 1939, 14, 69—73).—Mathematical relationships are given correlating various factors which affect the reaction of C₂H₂ with H₂SO₄ under various conditions. F. R.

Reactions in concentrated sulphuric acid. XVI. Selenium and tellurium as catalysts.—See A., 1939, I, 528.

Chemical methods of concentrating radioactive halogens.—See A., 1939, I, 532.

Fluorinated derivatives of propane. III. A. L. HENNE and M. W. RENOLL (J. Amer. Chem. Soc., 1939, 61, 2489—2491; cf. A., 1938, II, 467).—Previous conclusions on the course of fluorination of C₃Cl₈ and C₃HCl₇ are borne out and expanded. Structures of F₃-derivatives are proved. Probable structures are assigned to F₄-derivatives, partly on the basis of m.p. Fluorination of C₂Cl₅-CClF₂ or CCl₂(CCl₂F)₂ yields only $\alpha\alpha\beta\gamma$ -pentachloro- $\alpha\gamma\gamma$ -trifluoropropane, m.p. -4.9°, b.p. 152.3°, which in turn

yields $\alpha\beta\beta\gamma$ -tetrachloro- $\alpha\alpha\gamma\gamma$ -tetrafluoropropane, m.p. -42.9°, b.p. 112.0°. CHCl(CCl₂F)₂ yields, with much decomp., $\alpha\alpha\beta\gamma$ -tetrachloro- $\alpha\gamma\gamma$ -trifluoropropane, b.p. 128.7°, converted by alcoholic alkali into CHCl(CO₂Et)₂, decomposed by Cl₂ in light, and on further fluorination yielding impure CHCl(CClF₂)₂. CHCl₂-CCl₂-CClF₂ yields $\alpha\alpha\beta\gamma$ -tetrachloro- $\beta\gamma\gamma$ -trifluoropropane (I), b.p. 129.8°, which at high temp. affords, with decomp., $\alpha\alpha\beta$ -trichloro- $\beta\gamma\gamma\gamma$ -tetrafluoropropane (II), b.p. 89.8°. Chlorination of (I) gives $\alpha\alpha\alpha\beta\gamma$ -pentachloro- $\beta\gamma\gamma$ -trifluoropropane, m.p. -14.8°, b.p. 153.3°; that of (II) yields $\alpha\alpha\alpha\beta$ -tetrachloro- $\beta\gamma\gamma\gamma$ -tetrafluoropropane, m.p. -15.8°, b.p. 112.3°, which with Zn-EtOH yields α -dichloro- $\beta\gamma\gamma\gamma$ -tetrafluoro- Δ^2 -propene, b.p. 43.5° (dibromide, m.p. 35.5—37°, b.p. 154°). R. S. C.

Pure ethyl alcohol for absorption spectrophotometry.—See A., 1939, I, 582.

Aromatisation of fatty alcohols. V. I. KOMAREWSKY, C. H. RIESZ, and G. THEODOS (J. Amer. Chem. Soc., 1939, 61, 2525—2527).—When passed over Cr₂O₃-Al₂O₃ at 450—500°, aliphatic alcohols undergo successive dehydration (very rapid) and cyclisation-dehydrogenation. Thus, *n*-C₇H₁₅-OH or CHPr^a₂-OH yields PhMe; *n*-C₈H₁₃-OH gives C₆H₆; *n*-C₈H₁₇-OH gives PhEt (4.5%), PhMe (3%); by fission of PhEt), *o*-, *m*-, (trace), and *p*-xylene (7%); by isomerisation of PhEt), and higher aromatic compounds (32.7%). H₂, CO₂, and CO are also determined; production of CO and CO₂ indicates aldehyde formation. Approx. heats of activation for aromatisation and formation of CO, respectively, are *n*-C₇H₁₅-OH 59,700, —; CHPr^a₂-OH 57,600, 31,100; *n*-C₈H₁₃-OH 62,000, 14,200 kg.-cal. R. S. C.

Interconversion of crotyl alcohol and methylvinylcarbinol in aqueous sulphuric acid. W. G. YOUNG, K. NOZAKI, and (MISS) R. WARNER (J. Amer. Chem. Soc., 1939, 61, 2564—2565).—CHMe:CH-CH₂-OH and CH₃:CH-CHMe-OH are interconvertible by 3.7—7.4*N*-H₂SO₄ at room temp., some ether also being formed. The relative rates of the reactions depend on the concn. of the acid. R. S. C.

[Tri]chloro[*iso*]butanol. A. G. FISHBURN and H. B. WATSON (J. Amer. Pharm. Assoc., 1939, 28, 491—493).—OH-CMe₂-CCl₃ (+0.5H₂O), m.p. 77° (anhyd., m.p. 96.2°), is prepared by interaction of COMe₂ (100 g.), CHCl₃ (40 g.), and KOH (7 g. in saturated EtOH solution) for 15 min.; KCl is removed by filtration and COMe₂ + CHCl₃ by distillation, H₂O being added to the residue. The yield (calc. on CHCl₃) is 25% of theory. F. O. H.

Preparation of unsaturated higher alcohols. III. S. KOMORI (J. Soc. Chem. Ind. Japan, 1939,

42, 246—247B).—The reduction of the Et ester of the acids from rice oil and of Et erucate has been studied at temp. varying between 310° and 343° in the presence of Mg—Cr, Cd—Cr (I), Hg—Cr, Sr—Cr, Co—Cr (II), and Mn—Cr (all as oxides) obtained by decomp. of the requisite metallic chromate. (I) and (II) are excellent for the hydrogenation of an unsaturated fatty ester to a corresponding unsaturated alcohol.

H. W.

Partly *O*-methylated hexitols. III. Synthesis of $\alpha\gamma\delta\epsilon$ -tetramethyl-*l*-rhamnitol. R. S. TIPSON and P. A. LEVENE (J. Biol. Chem., 1939, 130, 235—242; cf. A., 1939, II, 466).—3 : 4-Dimethyl-1 : 2-methylorthoacetyl-*l*-rhamnose (modified prep.), m.p. 67—68°, $[\alpha]_D^{25} +40.6^\circ$ in H_2O , and boiling 0.5*N*-HCl give 2 : 3-dimethyl-*l*-rhamnose, new m.p. 102—103°, b.p. 99°/0.1 mm., reduced by H_2 —Raney Ni at 125°/1650 lb. in H_2O to $\gamma\delta$ -dimethyl-*l*-rhamnitol, m.p. 105°, $[\alpha]_D^{25} -25.5^\circ$ in abs. EtOH. H_2SO_4 and anhyd. $CuSO_4$ in $COMe_2$ then give $\beta\gamma$ -dimethyl- $\alpha\beta$ -isopropylidene-*l*-rhamnitol, b.p. 73°/0.1 mm., $[\alpha]_D^{25} -8.2^\circ$ in $COMe_2$, converted by MeI - Ag_2O into the $\gamma\delta\epsilon$ - Me_3C derivative, b.p. 64°/0.25 mm., $[\alpha]_D^{25} -6.6^\circ$ in $COMe_2$, which is hydrolysed by boiling 0.2*N*- H_2SO_4 to $\gamma\delta\epsilon$ -trimethyl-*l*-rhamnitol, b.p. 99—100°/0.1 mm., $[\alpha]_D^{25} -14.8^\circ$ in abs. MeOH. CPh_3Cl and then $BzCl$ in C_5H_5N convert this into the α - CPh_3 ether β -benzoate, a syrup, which in boiling $AcOH$ - H_2O (4 : 1) yields $\gamma\delta\epsilon$ -trimethyl-*l*-rhamnitol β -benzoate, b.p. 140°/0.1 mm., $[\alpha]_D^{25} -16.4^\circ$ in $COMe_2$ (and some $\alpha\beta$ -dibenzoate, b.p. 145—170°/0.1 mm., $[\alpha]_D^{25} -20.5^\circ$ in $COMe_2$), converted by Ag_2O - MeI into $\alpha\gamma\delta\epsilon$ -tetramethyl-*l*-rhamnitol β -benzoate, b.p. 130°/0.1 mm., $[\alpha]_D^{25} -9.1^\circ$ in $COMe_2$, and thence by boiling 0.4*N*- $Ba(OH)_2$ into $\alpha\gamma\delta\epsilon$ -tetramethyl-*l*-rhamnitol, b.p. 87°/0.25 mm., $[\alpha]_D^{25} -8.1^\circ$ in abs. EtOH. R. S. C.

Structure of the diisopropylidenedulcitol. R. M. HANN, W. D. MACLAY, and C. S. HUDSON (J. Amer. Chem. Soc., 1939, 61, 2432—2442).—To avoid ambiguity, dulcitol is numbered as *D,L*-galactitol. α - (I) and β -Diisopropylidenedulcitol (II) are shown to be structural isomerides, containing 1 and 2 primary OH, respectively. $OH \cdot C \cdot C \cdot OH$ is absent from (I) and (II), as neither is affected by aq. $NaIO_4$ or $Pb(OAc)_4$ in $AcOH$ unless hydrolysis, e.g., by keeping or heat, occurs. 0.4*M*- HIO_4 removes $COMe_2$ and thus oxidises (I) and (II). With Ac_2O - C_5H_5N , (II) yields the $\alpha\zeta$ -diacetate (III), m.p. 134°, which, owing to its insolubility, is useful for separating (I) and (II) and readily regenerates (II) by $NaOMe$ or $Ba(OMe)_2$. The $\alpha\zeta$ -(CPh_3)₂ ether, m.p. 233—234°, of (II) is prepared. The $\alpha\zeta$ -di-*p*-toluenesulphonate, m.p. 165—166° of (II) and NaI in hot $COMe_2$ give the $\alpha\zeta$ -di-iodide, m.p. 108—109°, confirming the free OH at α and ζ positions. Dulcitol " β "-dibenzoate (IV), previously called the " α "-dibenzoate, yields dulcitol $\alpha\zeta$ -dibenzoate $\beta\gamma\delta\epsilon$ -tetra-acetate, m.p. 225—226°. Hot 9% $AcOH$ hydrolyses (III) to dulcitol $\alpha\zeta$ -diacetate, m.p. 167—168°, which consumes 3 $Pb(OAc)_4$ in $AcOH$ and with $NaIO_4$ yields 2 HCO_2H . $Pb(OAc)_4$ similarly oxidises (IV) as expected to $OBz \cdot CH_2 \cdot CHO$ (isolated as semicarbazone or acid). (I) yields similarly $\beta\gamma\epsilon\zeta$ -diisopropylidene-*D,L*-galactitol $\alpha\delta$ -diacetate, m.p. 89°, $\alpha\delta$ -di-*p*-toluenesulphonate, m.p. 101°, and α -iodide δ -*p*-toluenesulphonate, m.p. 120—121°; it leads to

D,L-galactitol $\alpha\delta$ -dibenzoate, m.p. 170—171°, resolidifies, remelts 202—203° [transformation into (IV)] [consumes 2 $Pb(OAc)_4$ or 2 $NaIO_4$ (gives only a trace of HCO_2H)], and $\alpha\delta$ -dibenzoate $\beta\gamma\epsilon\zeta$ -tetra-acetate, m.p. 113°. With CPh_3Cl in C_5H_5N , followed by Ac_2O , (I) gives $\beta\gamma\epsilon\zeta$ -diisopropylidene-*D,L*-galactitol δ -acetate α - CPh_3 ether, m.p. 107—108°. The dibenzoate (prep. by $BzCl$ -quinoline) (V), m.p. 183—184°, of (II) with hot 80% $AcOH$ gives (IV), new m.p. 209°. With $BzCl$ in quinoline, (I) gives 66% of (IV) and 11% of $\beta\gamma\epsilon\zeta$ -diisopropylidene-*D,L*-galactitol $\alpha\delta$ -dibenzoate, m.p. 82—83°, previously called the " β "-dibenzoate; the migration of $COMe_2$ is catalysed by quinoline (or, less well, C_5H_5N) hydrochloride. The structures of (IV) and its isomerides are confirmed by debenzoylation by $NaOMe$. M.p. are corr. R. S. C.

Oxidation of ethyl disulphide by hypobromite ion.—See A., 1939, I, 527.

Di(carbethoxymethanesulphonyl)dialkylmethanes. R. L. SHRINER, J. M. CROSS, and E. H. DOBRATZ (J. Amer. Chem. Soc., 1939, 61, 2001—2003).—The CO_2Et of $CALK_2(SO_2 \cdot CH_2 \cdot CO_2Et)_2$ destroys the toxic and hypnotic actions of the compounds. $SH \cdot CH_2 \cdot CO_2H$, $COAlk_2$, and HCl at $<0^\circ$ give 82—96% of $\beta\beta$ -di(carboxymethylthiol)-*n*-propane, m.p. 134—135°, $\gamma\gamma$ -di(carboxymethylthiol)-*n*-pentane, m.p. 125—126°, $\delta\delta$ -di(carboxymethylthiol)-*n*-heptane, m.p. 133—134°, and $\epsilon\epsilon$ -di(carboxymethylthiol)-*n*-nonane, m.p. 86—87°, converted by HCl , abs. EtOH; and anhyd. $MgSO_4$ into the *Et* esters, b.p. (I) 152—153°/1.8 mm., 162—163°/2 mm., 178—179°/3 mm., and 183—184°/3 mm., respectively. These esters are very readily hydrolysed by acid, and, when distilled give, except (I), $SH \cdot CH_2 \cdot CO_2Et$ ($HgCl$ derivative, new m.p. 105°) and γ -carbethoxymethylthiol- Δ^8 -*n*-pentene, b.p. 78.5°/2 mm., δ -carbethoxymethylthiol- Δ^7 -*n*-heptene, b.p. 90°/1.8 mm., and ϵ -carbethoxymethylthiol- Δ^6 -*n*-nonene, b.p. 108°/1.8 mm., respectively. Addition of solid $KMnO_4$ to 10% H_2SO_4 and the esters in CCl_4 (not other methods) gives 32—42% of $\beta\beta$ -di(carbethoxymethanesulphonyl)-*n*-propane, m.p. 84—85°, $\gamma\gamma$ -di(carbethoxymethanesulphonyl)-*n*-pentane, m.p. 73—74°, $\delta\delta$ -di(carbethoxymethanesulphonyl)-*n*-heptane, m.p. 90—91°, and $\epsilon\epsilon$ -di(carbethoxymethanesulphonyl)-*n*-nonane, m.p. 74—75°, some hydrolysis also occurring. M.p. are corr. R. S. C.

Application of high temperatures in preparative organic work. A. J. VAN PELT, jun. (Chem. Weekblad, 1939, 36, 613—614).—A review of the recent work of Wibaut *et al.* on the high-temp. halogenation of C_5H_5N and quinoline and the pyrolysis of various acetates. S. C.

Effect of the silent electric discharge on the synthesis of monochloroacetic acid. Y. ISOMURA (Bull. Chem. Soc. Japan, 1939, 14, 258—270).—In the prep. of $CH_2Cl \cdot CO_2H$ (I) from $AcOH$ and Cl_2 using red P as a catalyst, activation of the Cl_2 by the silent electric discharge gives an increase of 15—100% in the yield as compared with activation by direct sunlight. With Brückner's (B., 1928, 254) catalyst (I + red P + PCl_5 ; 2 : 2 : 1) and solar activation of the Cl_2 a yield of 66% is obtained but it is difficult to remove all the I from the product on distillation.

However, by reducing the amount of I in the catalyst to 0.1–0.2 part and activating the Cl_2 by the silent electric discharge the yield is increased to 80% and the I can be eliminated by distillation at 180–190°. With red P alone as catalyst large amounts of AcCl are formed and the P does not act simply as a carrier of Cl_2 . The equation $2\text{P} + \text{AcOH} + 9\text{Cl}_2 = 2\text{AcCl} + 6\text{HCl} + 4(\text{I}) + 2\text{POCl}_3$ is therefore proposed instead of $\text{AcOH} + \text{Cl}_2 = (\text{I}) + \text{HCl}$, which appears to apply with the more complex catalyst. T. H. G.

Rate of hydration of crotonic acid. Rate of dehydration of β -hydroxybutyric acid. Equilibrium between these acids in dilute aqueous solution.—See A., 1939, I, 570.

Chromatographic separation of palmitic and stearic acids from their mixture with oleic acid. C. MANUNTA (Helv. Chim. Acta, 1939, 22, 1156–1160).—The mixture, dissolved in light petroleum, is adsorbed on $\text{MgSO}_4 \cdot 0.5\text{H}_2\text{O}$ or franconite and the column is developed by washing with light petroleum. Division of the column, extraction of the parts by Et_2O , and repeated chromatographic separation of the fractions thus obtained yields fairly pure palmitic (I) and stearic (II) acids. (I) is more strongly adsorbed than is (II). F. O. H.

Intermolecular oxidation of linoleic acid. M. BRAMBILLA (Annali Chim. Appl., 1939, 29, 303–314; cf. A., 1939, II, 47).—Linoleic acid, heated to 325° in N_2 , yields H_2O , CO_2 , EtCO_2H , PrCO_2H , hexoic, glutaric, and sebacic acid, and an unsaponifiable, carbonaceous residue which, on fractionation, affords $\text{C}_{10}\text{H}_{20}$, $\text{C}_{14}\text{H}_{28}$, $\text{C}_{16}\text{H}_{32}$, $\text{C}_{20}\text{H}_{40}$, $\text{C}_{25}\text{H}_{54}$, and $\text{C}_{32}\text{H}_{62}$. The mechanism of the degradation is discussed. F. O. H.

Acid, $\text{C}_{15}\text{H}_{22}\text{O}_3$, m.p. 118.5°, and lactone, $\text{C}_{15}\text{H}_{18}\text{O}_2$, m.p. 60.5°, from oil of kostus root.—See A., 1939, III, 950.

Improved [organic] procedures. K. M. SEYMOUR (J. Chem. Educ., 1939, 16, 285–287).—Directions for the prep. of $\text{H}_2\text{C}_2\text{O}_4$ from $(\text{CH}_2\text{OH})_2$ and HNO_3 are given. Advantages of using $(\text{CH}_2\text{Cl})_2$ instead of ethers as a solvent are pointed out. In the prep. of NH_2Ph by Degering's method (A., 1936, 1359) the yield is much increased by substituting $(\text{CH}_2\text{Cl})_2$ for the ether. An improved method for the prep. of NH_2Ac is described. L. S. T.

Polynuclear complex chromioxalates.—See A., 1939, I, 575.

Itaconic acid, metabolic product of *Aspergillus terreus*.—See A., 1939, III, 1010.

Influence of temperature on aqueous solutions of l-malic acid.—See A., 1939, I, 564.

Dibenzyl sebacate. R. E. BURNETT and J. J. RUSSELL (J. Amer. Chem. Soc., 1939, 61, 2246).— $(\text{CH}_2\text{Ph})_2$ sebacate, m.p. 28.3°, b.p. 257° (uncorr.)/4 mm., is prepared from the acid and alcohol. R. S. C.

Synthesis of aldehydes by Stephen's method. J. W. WILLIAMS (J. Amer. Chem. Soc., 1939, 61, 2248–2249).—Stephen's method gives the following yields of RCHO : $\text{R} = \text{Ph}$ 97, β - 91 and α - C_{10}H_7 7, G G* (A., II.)

p - 77 and o -tolyl 9, CH_2Ph 33, *iso*- C_7H_{15} 31%, and $\text{OH}[(\text{CH}_2)_2]_0$. R. S. C.

Formation of acetaldehyde from succinic acid by quinone catalysis.—See A., 1939, III, 939.

Reversed aldol condensation. H. FRAENKEL-CONRAT (Science, 1939, 90, 114).—On digestion with H_2O at 37° α -keto- γ -acetoxyvaleric acid dissolves within a few days forming AcCO_2H , AcOH , and MeCHO . The next higher homologue behaves similarly, but aldol, acetaldol, $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COMe}$ are stable under these conditions. An acid p_H of the solution or an acid group in the mol. appears to be necessary for the decomp., as well as a $\text{CO}\beta$ to an esterified OH . These reactions indicate that the readily fermentable hexose diphosphate is a ketose, with one PO_4 in position 4. L. S. T.

Keten generator. C. H. LI (Science, 1939, 90, 143).—In the apparatus described and illustrated, COMe_2 vapour is decomposed by a W filament at bright-red heat, and unchanged COMe_2 and keten polymerides are removed by a condenser and a special trap immersed in ice + salt. Keten is passed into the solution through a sintered-glass plate. L. S. T.

Oxidation of simple sugars. A. QUARTAROLI and A. RATTU (Annali Chim. Appl., 1939, 29, 296–302).—The oxidation by O_2 of monosaccharides in presence of FeSO_4 involves the formation of FeO_2 ; this reacts with the acceptor with production of Fe_2O_3 . The oxidation product, if in sufficient concn., prevents pptn. of basic Fe salts. Examples of such systems in buffered solution are described. F. O. H.

Preparation of fully methylated carbohydrates and their derivatives. E. PACSU and S. M. TRISTER (J. Amer. Chem. Soc., 1939, 61, 2442–2444).—Methylation of carbohydrates is difficult owing to incomplete reaction of CH_2OH . Sugars, partly methylated by Me_2SO_4 or $\text{MeI}\text{--Ag}_2\text{O}$, are fully methylated thereafter by one treatment with Na in Et_2O , PhMe , etc., followed by MeI . Prep. of octamethylsucrose is described. R. S. C.

Tetrose sugars. IV. Structure of a methyl-d-erythroside. Mutarotation of d-arabinose-oxime. R. C. HOCKETT and C. W. MAYNARD, jun. (J. Amer. Chem. Soc., 1939, 61, 2111–2115; cf. A., 1938, II, 126).—*d*-Arabinoseoxime, m.p. 136–137°, $[\alpha]_D^{20} -84^\circ \rightarrow$ (unimol.) -13.5° in H_2O , with Ac_2O NaOAc -dioxan or Ac_2O - $\text{C}_5\text{H}_5\text{N}$ gives *d*-arabonitrile tetra-acetate, m.p. 120–121° (corr.), $[\alpha]_D^{20} -33.3^\circ$ in CHCl_3 , and thence *d*-erythrosediacetamide. With 0.6*N*- H_2SO_4 at 100° (for 0.1*N*- H_2SO_4 $k = 0.0175$), this gives syrupy *d*-erythrose, which with 1% HCl - MeOH gives methyl-d-erythroside (I), b.p. 78–98°/1–2 mm., $[\alpha]_D^{20}$ variable, -5.34° to 0° in CHCl_3 . Me_2SO_4 -60% NaOH converts (I) into dimethylmethyl-d-erythroside, b.p. 135–145°/1–2 mm., oxidised by HNO_3 (d 1.2) at 85–90° to *meso*- $[\text{CH}(\text{OMe})\cdot\text{CO}_2\text{H}]_2$. 1 mol. of $\text{Pb}(\text{OAc})_4$ is consumed by (I) in CHCl_3 , the reaction having the fast rate characteristic of *cis*-diols and yielding with $\text{Br}\text{--SrCO}_3$ *Sr D'*-methoxydiglycollate (58% of α - and 42% of β -), $[\alpha]_D^{20} -8.94^\circ$ in H_2O . R. S. C.

Quantitative formation of furfuraldehyde and methylfurfuraldehyde from pentoses and methyl-pentoses. E. E. HUGHES and S. F. ACREE (J. Res. Nat. Bur. Stand., 1939, 23, 293—298; cf. A., 1939, II, 7).—During rapid steam-distillation in 12% HCl saturated with NaCl the conversion of arabinose and rhamnose is slower than that of xylose, but theoretical yields of furfuraldehyde (I) and methylfurfuraldehyde, respectively, are obtained. Addition of salts to raise the distillation temp. to $>112^\circ$ increases the initial rate of formation of (I) from xylose and arabinose, but decreases the yields. To ensure complete conversion it is desirable to take samples >0.1 g. when determining pentoses by this method. J. W. S.

Action of silver salts of organic acids on bromoacetyl sugars. New form of *l*-rhamnose tetraacetate. R. S. TIPSON (J. Biol. Chem., 1939, 130, 55—59).—AgOAc or AgOBz with bromoacetyl derivatives of sugars gives compounds having *trans*-OAcyl on C₍₁₎ and C₍₂₎. Thus are obtained *l*-rhamnose tetraacetate, b.p. 129—130°/0.1 mm., $[\alpha]_D^{25} -61.7^\circ$ in CHCl₃, and *d*-xylose 1-benzoate triacetate, m.p. 147—147.5°, $[\alpha]_D^{25} -70.3^\circ$ in CHCl₃. R. S. C.

Mutarotation of tetramethyl- α -*d*-glucopyranose and -mannopyranose. B. C. HENDRICKS and R. E. RUNDLE (J. Amer. Chem. Soc., 1939, 61, 2103—2105).—The mutarotations of tetramethyl- α -*d*-glucose and -mannose at 0° and 25° are first-order reactions. Heats of activation are similar to those of the non-methylated sugars. R. S. C.

Substitution of glucose in position 4. II. β -Benzylglucoside 2:3-diacetate and its derivatives. A. L. RAYMOND, R. S. TIPSON, and P. A. LEVENE (J. Biol. Chem., 1939, 130, 47—54; cf. A., 1933, 54).— β -Benzylglucoside [prep. from glucosidyl bromide tetraacetate by CH₃Ph.OH, followed by Ba(OMe)₂-MeOH] with PhCHO and ZnCl₂ and then Ac₂O-C₅H₅N gives 4:6-benzylidene- β -benzylglucoside 2:3-diacetate, m.p. 208—209°, $[\alpha]_D^{25} -108.4^\circ$ in CHCl₃, hydrolysed by 0.25N-HCl to β -benzylglucoside 2:3-diacetate (I), m.p. 116—117°, $[\alpha]_D^{25} -67.4^\circ$ in COMe₂, $[\alpha]_D^{25} -85.9^\circ$ in EtOH. With *p*-C₆H₄Me-SO₂Cl-C₅H₅N, (I) gives β -benzylglucoside 2:3-diacetate 4:6-di-*p*-toluenesulphonate, m.p. 143—144°, $[\alpha]_D^{25} -34.0^\circ$ in COMe₂, which with NaI-COMe₂ at 100° gives β -benzylglucoside 6-iodide 2:3-diacetate 4-*p*-toluenesulphonate, m.p. 125—126°, $[\alpha]_D^{25} -67.4^\circ$ in COMe₂. Ac₂O-CHCl₃ at room temp. converts (I) into the 2:3:6-triacetate, cryst., b.p. 190—195°/0.1 mm., $[\alpha]_D^{25} -55.4^\circ$ to -57.8° in COMe₂. Addition of *p*-C₆H₄Me-SO₂Cl in CHCl₃ to (I) in C₅H₅N gives β -benzylglucoside 2:3-diacetate 6-*p*-toluenesulphonate, cryst. R. S. C.

isoPropylidene derivatives of the mercaptals of monosaccharides. IV. 4:5-isoPropylidene derivative of the dibenzyl mercaptan and of the dimethyl acetal of *d*-galactose. E. PACSU, S. M. TRISTER, and J. W. GREEN (J. Amer. Chem. Soc., 1939, 61, 2444—2448).—Prop. of 4:5- (I), m.p. 102.5—103°, $[\alpha]_D^{25} +31.0^\circ$ in CHCl₃, and (?) 5:6-iso-propylidenegalactose (CH₂Ph)₂ mercaptal, m.p. 112.5°, $[\alpha]_D^{25} +17.4^\circ$ in CHCl₃, is detailed (cf. A., 1930, 197; 1936, 1491). The structure of (I) follows from form-

ation of a CPh₃ ether, amorphous, and from the following reactions. With HgCl₂-HgO-MeOH, (I) gives 4:5-iso-propylidenegalactose Me₂ acetal (II), m.p. 125—126°, $[\alpha]_D^{25} +37.4^\circ$ in H₂O (2:3:6-triacetate, m.p. 55°, $[\alpha]_D^{25} +17.8^\circ$ in CHCl₃), which is incompletely methylated by MeI-Ag₂O (5 treatments), but after final treatment with Na-MeI yields the syrupy 2:3:6-Me₃ ether. Hydrolysis by 0.05N-HBr at 60—70° and subsequent oxidation by Br at 35—40° then gives 2:3:6-trimethyl- γ -galactonolactone, m.p. 97—98°, $[\alpha] -32.9^\circ \rightarrow -21.3^\circ$ in H₂O in 3 days, which consumes 1 HIO₄. 1 HIO₄ is consumed also by (II) to yield glyoxal (isolated as bisphenylhydrazone) and 2:3-iso-propylidene-*d*-threose, characterised by hydrolysis to *d*-threose (osazone) and oxidation thereof to *d*-threonic acid (brucine salt) and thence to *l*-[CH(OH)-CO₂H]₂. R. S. C.

Cardiac glycosides. XV. Periplocin, the genuine cardiac glycoside of *Periploca graeca*. A. STOLL and J. RENZ (Helv. Chim. Acta, 1939, 22, 1193—1208).—The stems and bark of *P. graeca* are extracted with EtOH and the extract is evaporated to dryness in vac. The residue is treated with Pb(OH)₂ and then with H₂O-EtOH-CHCl₃ in varied proportions. The crude glycoside is transformed by Ac₂O and C₅H₅N at room temp. into periplocin tetraacetate, m.p. 195°, $[\alpha]_D^{25} +20.0^\circ$ in abs. EtOH, which is hydrolysed by the requisite amount of Ba(OMe)₂-MeOH to periplocin, (I), C₃₆H₅₆O₁₃, m.p. 209° when slowly heated or m.p. 224° (decomp.) in bath preheated to 200°, $[\alpha]_D^{25} +22.9^\circ$ in MeOH, $+23^\circ$ in EtOH. Hydrolysis of (I) with 0.1N-H₂SO₄ at 25° and then at 40—50° yields periplogenin, C₂₃H₃₄O₈, m.p. 232° after softening at 165—170°, $[\alpha]_D^{25} +29.8^\circ$ in MeOH, and periphlobiose, C₁₃H₂₄O₉, decomp. 160—170° after softening at $\sim 120^\circ$ greatly dependent on the mode of heating and moisture content, $[\alpha]_D^{25} +30.8^\circ$ in H₂O (*c* = 0.276). Strophanthobiase hydrolyses (I) rather more readily than it does *k*-strophanthin- β , giving glucose and periplocymarin, C₃₀H₄₆O₈, m.p. 143—145° after softening at 135°, $[\alpha]_D^{25} +30.2^\circ$ in 95% EtOH, $+27.6^\circ$ in MeOH. Periphlobiose pentaacetate, m.p. 184°, $[\alpha]_D^{25} +19.5^\circ$ in CHCl₃ (*c* = 0.353), differs from strophanthobiase pentaacetate, m.p. 162°, $[\alpha]_D^{25} +13.2^\circ$ in CHCl₃, although each sugar is formed from glucose and cymarose. H. W.

***p*-Nitrophenol- β -galactoside, m.p. 170°, $[\alpha]_D^{25} -74.7^\circ$ in H₂O (tetra-acetate, m.p. 138°).**—See A., 1939, III, 940.

Quercetin-3-galactoside, $+1.5\text{H}_2\text{O}$, m.p. 235—237°, $[\alpha]_D^{25} -51.6^\circ$.—See A., 1939, III, 951.

Molecular size of starch by the mercaptalation method. M. L. WOLFROM, D. R. MYERS, and E. N. LASSETTRE (J. Amer. Chem. Soc., 1939, 61, 2172—2174).—By hydrolysis of potato starch with conc. HCl at 0° in presence of EtSH (excess), isolation of the product as acetate, and S determination, it is shown that the product contains 17 glucose units after 0.5 and 2 units after 26 hr. $[\alpha]$ of mixtures of the starch and HCl at 0° are recorded at various times. Graphic analysis indicates 20 ± 4 glucose units per mol. of the original starch. R. S. C.

Enzyme-protein complex which phosphorylates glycogen : reversible enzymic synthesis of glycogen.—See A., 1939, III, 940.

Polysaccharides. XXXII. Molecular constitution of rice starch. E. L. HIRST and G. T. YOUNG. *Examination in the ultracentrifuge.* J. ST. L. PHILPOT (J.C.S., 1939, 1471—1481, 1481—1482).—Methylstarch (I) prepared by direct methylation ($\text{Me}_2\text{SO}_4\text{--NaOH}$) in air or N_2 , or prepared via the acetate, shows mol. wts., determined by η in *m*-cresol, varying from 175,000 to 600,000. Independently of the mode of prep. of (I) and irrespective of the mol. wt., the method of end-group assay shows a const. % of tetramethylglucose (II) and indicates a repeating unit of 24—30 glucose units. The observed proportion of (II) cannot be explained by random hydrolysis of long chains of similarly united residues and it is concluded that viscous methylstarches are composed of a large no. of repeating units joined together laterally, forming side-chains. Thus, a viscous methylstarch (mol. wt. $\sim 500,000$), disaggregated by heating with $\text{H}_2\text{C}_2\text{O}_4$ in $\text{COMe}_2\text{--H}_2\text{O}$ and methylated ($\text{Me}_2\text{SO}_4\text{--NaOH}$), yields a substance (III) of mol. wt. $\sim 20,000$ (by osmotic pressure and ultracentrifuge measurements) corresponding with 3 repeating units (90 glucose residues). On hydrolysis (AcOH--HCl) this material gives the same yield of (II) as do the viscous methylstarches, but the yield of dimethylglucose is very small. From consideration of the conditions of the disaggregation process it is concluded that in the starch mol. the repeating units, each consisting of a chain of 30 glucose residues, are linked to a non-terminal glucose residue of another unit by primary valencies of the glycosidic type. The relationship between η and mol. wt. in the methylstarch series is discussed and an empirical method is suggested for the utilisation of η measurements in the determination of approx. mol. sizes.

Ultracentrifuge examination of (III) indicates that the material is essentially homogeneous, of min. mol. wt. 18,700, and that the mols. are spherical in shape.

J. D. R.

Constitution of the mucilage from the bark of *Ulmus fulva* (slippery elm mucilage). I. Aldobionic acid obtained by hydrolysis of the mucilage. R. E. GILL, E. L. HIRST, and J. K. N. JONES (J.C.S., 1939, 1469—1471).—Partial hydrolysis ($\text{N--H}_2\text{SO}_4$) of the mucilage extracted by H_2O from the inner bark yields (as *Ba* salt) an aldobionic acid (I), which when methylated (TIOH--MeI followed by $\text{MeI--Ag}_2\text{O}$) and hydrolysed yields $\alpha\beta\gamma$ -trimethyl-*d*-galacturonic acid and 3 : 4-dimethyl-*L*-rhamnose; (I) is therefore 2-*d*-galacturonido-*L*-rhamnose, identical with the aldobionic acid from flax-seed mucilage (cf. Tipson *et al.*, A., 1939, II, 298).

J. D. R.

Constitution of damson gum. II. Hydrolysis products from methylated degraded (arabinose-free) damson gum. E. L. HIRST and J. K. N. JONES (J.C.S., 1939, 1482—1490).—The polysaccharide *A* from damson gum (cf. A., 1938, II, 394) on repeated methylation (TIOH--MeI and finally $\text{MeI--Ag}_2\text{O}$) yields a methylated polysaccharide (I) containing uronic anhydride, purified by fractional pptn. by light petroleum from CHCl_3 . Hydro-

lysis of (I) with N--HCl followed by treatment with HCl--MeOH and fractional distillation yields 2 : 3 : 4-trimethylmethyl-*d*-xylose ($\frac{1}{6}$ part), tetramethylmethyl-*d*-galactose (1 part), 2 : 3 : 4- (1 part) and 2 : 4 : 6-trimethylmethyl-*d*-galactose (1 part) (*anilide*, m.p. 179° , $[\alpha]_D^{25} -92^\circ$ in $\text{COMe}_2 \rightarrow +38^\circ$ in 22 hr.), and 4 : 6-dimethylmethyl-*d*-galactose (1 part) (*anilide*, m.p. 207° , $[\alpha]_D^{25} -174^\circ$ in $\text{C}_5\text{H}_5\text{N}$), which on oxidation (Br) yields γ -dimethyl-*d*-galactonolactone, a syrup, $[\alpha]_D^{25} +78^\circ$ in MeOH , $+91^\circ$ in $\text{H}_2\text{O} \rightarrow +45^\circ$ in 60 hr., converted by liquid NH_3 into γ -dimethyl-*d*-galactonamide monohydrate, m.p. 164° , $[\alpha]_D^{25} +54^\circ$ in H_2O . From the acidic part of the hydrolysis products of (I) are isolated $\alpha\beta\gamma$ -trimethyl-*d*-glycuronic acid (1 part) and $\alpha\beta$ -dimethyl-*d*-glycuronic acid (1 part), which when oxidised (Br) and esterified yields dimethylsaccharolactone *Me ester*, m.p. 101° .

J. D. R.

Constitution of cellulose with special regard to hydrolytic experiments.—See A., 1939, I, 511.

Kinetics of thermal decomposition of methylamines.—See A., 1939, I, 528.

General synthesis of α -amino-acids by means of ethyl benzamidomalonate. C. A. REDEMANN and M. S. DUNN (J. Biol. Chem., 1939, 130, 341—348).— $\text{OH--N:C(CO}_2\text{Et)}_2$ (prep. by $\text{Bu}^+\text{O--NO}$) is reduced by $\text{H}_2\text{--Raney Ni}$ to $\text{NH}_2\text{--CH(CO}_2\text{Et)}_2$, which with BzCl in H_2O containing $\text{C}_5\text{H}_5\text{N}$ gives $\text{NHBz--CH(CO}_2\text{Et)}_2$, m.p. $73\text{--}74^\circ$ (lit., 61°). With NaOEt--EtOH , followed by an alkyl or aralkyl iodide, this gives the *C*-alkyl-ester, hydrolysed and decarboxylated, best by boiling HBr , to the $\alpha\text{--NH}_2$ -acid. Phenylalanine, leucine, aspartic acid, and valine are thus prepared. For serine and threonine the condensation with RI should be effected in C_6H_6 or PhMe etc. (no details given).

R. S. C.

Synthesis of α -aminopelargonic acid. T. B. JOHNSON (J. Amer. Chem. Soc., 1939, 61, 2485—2487).— $n\text{--C}_6\text{H}_{13}\text{--CHO}$, hydantoin, and NaOAc in AcOH give *n*-heptylidene-, m.p. $157\text{--}159^\circ$, reduced by SnCl_2 to *n*-heptyl-hydantoin, m.p. $142\text{--}143^\circ$, which, by prolonged boiling with aq. Ba(OH)_2 , gives α -aminononoic acid, decomp. $236\text{--}256^\circ$ (hydrochloride).

R. S. C.

(A) Stereoisomerides of γ -amino- β -hydroxybutyric acid. M. TOMITA and Y. SEIKI. (B) Stereoisomerides of isoserine. Y. SEIKI (J. Biochem. Japan, 1939, 30, 101—105, 107—112).—(A) X-Ray diagrams of *l*- and *d*- γ -amino- β -hydroxybutyric acid-I or of the *l*- and *d*-forms of acid-II are identical; that of acid-I, however, differs from that of acid-II (cf. A., 1927, 1058). Acid-II has a ring, and -I an open-chain, structure (cf. Bergmann and Lissitzin, A., 1930, 459).

(B) The conclusions of Tomita *et al.* (A., 1932, 1118) are confirmed by X-ray studies and the structure of the isomerides is further discussed.

F. O. H.

Racemisation of benzyl-L-cysteine. Preparation of *d*-cystine. J. L. WOOD and V. DU VIGNEAUD (J. Biol. Chem., 1939, 130, 109—114).—*d*-Cystine (I) is best prepared by treating *S*-benzyl-L-cysteine (prep. from *l*-cystine by Na, followed by CH_2PhCl , in liquid NH_3) with $\text{Ac}_2\text{O--NaOH}$ at $45\text{--}50^\circ$

and hydrolysing the resulting *dl*-N-Ac compound by HCl. *S*-Benzyl-*dl*-cysteine, m.p. 213–215°, thus produced is converted by Ac_2O in 90% HCO_2H at 55–60° into the N-CHO derivative, m.p. 136.5°, which is resolved by brucine to yield the d-salt, $[\alpha]_D^{25} -25^\circ$ in H_2O , and thence *S*-benzyl-d-cysteine, $[\alpha]_D^{25} -22.5^\circ$ in N-NaOH. Na in liquid NH_3 then yields (I), $[\alpha]_D^{25} +22.4^\circ$ in N-HCl. R. S. C.

Decomposition of cysteine in aqueous solution. J. I. ROUTH (J. Biol. Chem., 1939, 130, 297–304).—When boiled in air or N_2 with dil. aq. NaCl (0.48 g. per l.) cysteine (I) decomposes more slowly than cystine (II) (A., 1939, II, 11) but yields (II), H_2S , and NH_3 , with products similar to sulphenic and sulphinic acids which cause a progressive decrease in the p_{H} of the solutions during heating. The progressive decrease in the NH_2 -content and the non-formation of free S indicate that the mechanism of the decomp. of (I) differs from that of (II). J. W. S.

Conversion of methionine into cystine. Radioactive sulphur. H. TARVER and C. L. A. SCHMIDT (J. Biol. Chem., 1939, 130, 67–80).—S containing ^{35}S is converted successively into FeS , H_2S , $\text{CH}_2\text{Ph}\cdot\text{SH}$, $\text{CH}_2\text{Ph}\cdot\text{S}\cdot[\text{CH}_2]_2\cdot\text{Cl}$, *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot[\text{CH}_2]_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, *phthal-imidobenzylthiolmalonic acid*, m.p. 110–111° (decomp.; corr.), *S*-benzylhomocysteine, and methionine. When this methionine (but not Na_2SO_4 containing $\text{Na}_2^{35}\text{SO}_4$), is fed to or injected intravenously into rats, it is converted into radioactive cystine. The change probably proceeds thus: $\text{SH}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H} \rightarrow \text{SH}\cdot\text{CHMe}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H} \rightarrow \text{SH}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$. R. S. C.

Stability of the keto-acid from methionine. H. WAELSCH and E. BOREK (J. Amer. Chem. Soc., 1939, 61, 2252).—Deamination of methionine (I) by kidney slices gives a ketone (II), $\text{C}_5\text{H}_8\text{O}_3\text{S}$, isolated as *dinitrophenylhydrazone* (~20%), m.p. 149°. If the incubated solution is deproteinised and boiled in 2N-NaOH- N_2 , MeSH is formed (isolated as Hg salt) and must be derived from the (II) as (I) is stable to alkali. R. S. C.

Di-($\beta\gamma$ -dihydroxypropyl)oxamide and its nitration products. T. DOMAŃSKI and J. SKUDRZYK (Rocz. Chem., 1939, 19, 427–432).— $[\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}]_2$ (I) was obtained by the reactions: glycerol + HCl \rightarrow chlorohydrin (II) (+NaOH) \rightarrow glycidic (+ NH_3) \rightarrow $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ (III) (+ $\text{Et}_2\text{C}_2\text{O}_4$) \rightarrow (I); (II) + NH_3 \rightarrow (III) (+ $\text{H}_2\text{C}_2\text{O}_4$) \rightarrow oxalate \rightarrow (I). (I) nitrated (HNO_3 d 1.38, H_2SO_4 d 1.84) at $<10^\circ$ yields NN'-di-($\beta\gamma$ -dihydroxypropyl)oxamide tetranitrate, m.p. 142.5°. This is a strong explosive, of high stability. Its properties resemble those of $(\text{NO}_2\cdot\text{NMe}\cdot\text{CO})_2$. R. T.

Use of mercuric acetate in organic preparations. I. Mercury compounds of amides and imides. N. V. S. RAO and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 10, A, 1–5).—Good yields of pure *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NHg}$ (I) and $(\cdot\text{CH}_2\cdot\text{CO})_2\text{NHg}$ are quickly obtained from the respective imide and $\text{Hg}(\text{OAc})_2$ in EtOH. With 1 mol. of $\text{Hg}(\text{OAc})_2$ in EtOH, $\text{CO}(\text{NH}_2)_2$ gives *mercuricarbamide*, $\text{CO}(\text{NH})_2\text{Hg}$,

m.p. $>340^\circ$ (yellow at 230°) [which may replace (I) pharmaceutically], but with 2 mols. of $\text{Hg}(\text{OAc})_2$ gives *di(acetoxymercuri)carbamide*, $\text{CO}(\text{NH}\cdot\text{HgOAc})_2$, decomp. $\sim 270^\circ$. NH_2Ac and $\text{Hg}(\text{OAc})_2$ at 180° give Hg, AcOH, and a mixture. NH_2Ac (2 mols.) and $\text{Hg}(\text{OAc})_2$ (1 mol.) in EtOH give N-acetoxymercuri-acetamide, m.p. 195° (decomp.); larger proportions of $\text{Hg}(\text{OAc})_2$ give a product (Hg 72, N 3.9%), m.p. 225° (decomp.). R. S. C.

Attempts to prepare optically active ethyleneimine derivatives containing an asymmetric nitrogen atom. R. ADAMS and T. L. CAIRNS (J. Amer. Chem. Soc., 1939, 61, 2464–2467).—*p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}$ and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ in 10% NaOH at $50\text{--}70^\circ$ give *p*-bromobenzenesulphon- β -hydroxyethylamide (I), m.p. $93.5\text{--}95^\circ$, converted by SOCl_2 into the β -Cl-compound, m.p. $150\text{--}152.5^\circ$, which with hot, 1% KOH regenerates (I). *p*-Bromobenzenesulphon- β -hydroxyisobutylamide (II) (similarly prepared), m.p. $96.5\text{--}98^\circ$, is converted by 48% HBr into *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\cdot\text{NH}_2$ (III), by P_2O_5 into 4-*p*-bromobenzenesulphon-1 : 1 : 6 : 6- or -1 : 1 : 5 : 5-tetramethylmorpholide, m.p. $145\text{--}147^\circ$, with some (III), and by boiling, conc. HCl into *p*-bromobenzenesulphon- β -chloroisobutylamide (IV), m.p. $123\text{--}128^\circ$. 10% NaOH at 100° converts (IV) into (II) (~50%) and 1-*p*-bromobenzenesulphon-2 : 2-dimethylethyleneimine (46%), m.p. $79.5\text{--}81.5^\circ$; KOH-EtOH gives (II) and an oil. Distillation of $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NH}_2$ with aq. H_2SO_4 gives β -methylallylamine (V), b.p. $76.7\text{--}77.7^\circ/746$ mm. (*hydrochloride*, m.p. $190\text{--}191^\circ$; *picrate*, m.p. $202\text{--}206^\circ$; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2$, m.p. $74\text{--}76^\circ$, and *thiocarbamide* derivatives, m.p. $78\text{--}79^\circ$). $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{Cl}$ and *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$ at 150° give N- β -methylallylphthalimide, m.p. $88.5\text{--}90^\circ$, converted by N_2H_4 into (V). *p*-Bromobenzenesulphon- β -hydroxy- $\beta\beta$ -diphenylethylamide (VI), m.p. $151\text{--}153^\circ$, does not yield the β -Cl-compound; with SOCl_2 or, best, P_2O_5 in C_6H_6 it gives *p*-bromobenzenesulphon- $\beta\beta$ -diphenylvinylamide, m.p. $197\text{--}198^\circ$, oxidised by CrO_3 to COPh_2 . The camphor- and α -bromocamphor-sulphonamide analogues of (II) and the α -bromocamphorsulphonamide analogue of (VI) are oils. M.p. are corr. R. S. C.

Explosion of ethyl azide in presence of diethyl ether.—See A., 1939, I, 568.

Detection of chloride in chlorovinylarsine (lewisite). C. FROGER (Compt. rend., 1939, 209, 351).—Passage of $\text{CHCl}\cdot\text{CH}_2\cdot\text{AsCl}_2$ (I) vapour through Draeger's detector tube (SiO_2 gel) followed by a little $\text{Br}\cdot\text{H}_2\text{O}$ and aq. fluorescein shows an eosin-coloured region where Br has not reacted with (I). The reaction occurs only with high concns. of (I). (I) adsorbed on SiO_2 reacts with 1% OsO_4 to give a black ppt.; 25 mg. of (I) per cu.m. of air can be detected. EtOH, Et_2O , and COMe_2 do not react with OsO_4 ; acetaldehyde reacts. J. L. D.

[Coupling organic radicals by means of the Grignard reagent.] J. H. GARDNER and L. JOSEPH (J. Amer. Chem. Soc., 1939, 61, 2551–2552; cf. A., 1930, 76).— MgBu^tBr and AgBr give 37.5% of Bu^t_2 , and $\text{CHMeEt}\cdot\text{MgBr}$ gives 13% of $(\text{CHMeEt})_2$. No rearrangement occurs. R. S. C.

Introduction of racemic organic molecules into some optically active complex ions of cobalt and chromium.—See A., 1939, I, 576.

Relative dissymmetric synthesis and rotation-dispersion in cobaltic complexes of the α -amino-acids.—See A., 1939, I, 533.

Investigation of the isomeric dichlorobis-ethylenediaminocobaltic chlorides by means of a radioactive isotope of chlorine.—See A., 1939, I, 576.

New class of amines. Complex thiomolybdates and thionitrogenates.—See A., 1939, I, 532.

Complex compounds of platinum [chloride] and butadiene.—See A., 1939, I, 533.

Oxygen effect in the reaction of cyclopropane with bromine and with hydrogen bromide. M. S. KHARASCH, M. Z. FINEMAN, and F. R. MAYO (J. Amer. Chem. Soc., 1939, 61, 2139—2142).—In absence of O_2 , reaction of cyclopropane (I) and Br_2 is very slow in light or dark. O_2 , Bz_2O_2 , or ascaridole accelerates the reaction, particularly in the light. O_2 , Bz_2O_2 , o - $C_6H_4(OH)_2$, $O_2 + NHPh_2$, or H_2O accelerates the slow reaction of 0.1 mol. of HBr with (I), but o - $C_6H_4(OH)_2 + O_2$ has less effect than O_2 alone; light has little effect. A chain mechanism involving Br atoms is suggested for both reactions. O_2 or light has no effect on the reaction with 1 mol. of HBr , but o - $C_6H_4(OH)_2$, H_2O , $AcOH$, or $C_6H_4Me \cdot SH$ accelerates the reaction in absence of O_2 ; a competing non-at. mechanism is suggested. R. S. C.

Synthesis of antirachitic vitamins. I. Synthesis of γ -2-methylenecyclohexylidene- Δ^a -propene. N. A. MILAS and W. L. ALDERSON, jun. (J. Amer. Chem. Soc., 1939, 61, 2534—2537).—2-Dimethylaminomethylcyclohexanone (prep. described) and $CH_2:CH \cdot CH_2 \cdot MgBr$ in Et_2O give 2-dimethylaminomethyl-1-allylcyclohexanol (I), b.p. ~ 112 — $117^\circ/5$ mm. (acetate, b.p. 129 — $130^\circ/9$ mm.), the unstable bromide (prep. by PBr_3 in C_6H_6) of which is converted by KOH at $175^\circ/vac.$ into γ -2-dimethylaminomethylcyclohexylidene- Δ^a -propene, b.p. 126.5 — $128^\circ/10$ mm. (absorption max. at $236 m\mu$, mol. extinction coeff. 10,500), obtained also less well directly from (I) by various methods of dehydration ($KHSO_4$ gives a good yield of a rearranged product, b.p. 100 — $103^\circ/9$ mm.). The amine gives a methiodide, which, when treated with Ag_2O etc. and distilled at $60^\circ/5$ mm., gives γ -2-methylenecyclohexylidene- Δ^a -propene, b.p. 62 — $63^\circ/7$ mm. (absorbs 3 H_2). This has the unsaturated system of an antirachitic vitamin and has an absorption max. at $255 m\mu$. with a mol. extinction coeff. 19,000. R. S. C.

Reduction of diazonium salts to hydrocarbons with alkaline formaldehyde. R. Q. BREWSTER and J. A. POJE (J. Amer. Chem. Soc., 1939, 61, 2418—2419).—Addition of ArN_2Cl to aq. $NaOH \cdot CH_2O$ gives the ArH from the following NH_2Ar : NH_2Ph 60; o - and p - $C_6H_4Me \cdot NH_2$ 80; o - 75 and p - $OMe \cdot C_6H_4 \cdot NH_2$ 72; o - 75 and p - $OEt \cdot C_6H_4 \cdot NH_2$ 65; m -4- $C_6H_3Me_2 \cdot NH_2$ 80; p - 50 and o - $C_6H_4Cl \cdot NH_2$ 55; p - and o - $NH_2 \cdot C_6H_4 \cdot OPh$ 60; o - and p - $NH_2 \cdot C_6H_4 \cdot O \cdot C_6H_4Me \cdot p$

50; 2:5:1- $C_6H_3Cl_2 \cdot NH_2$ 10; o - $NH_2 \cdot C_6H_4 \cdot CO_2H$ 25; o - 20, m - 10, and p - $NO_2 \cdot C_6H_4 \cdot NH_2$ 10%. The method succeeds best when $EtOH$ fails and vice versa.

R. S. C.

Possible dimorphism of trinitrobenzene. T. URBANSKI and J. SIMON (Rocz. Chem., 1939, 19, 487—491).—Nitration of m - $C_6H_4(NO_2)_2$ with HNO_3 and 60% oleum gives s - $C_6H_3(NO_2)_3$ (I), m.p. 121° , or a substance, m.p. 61 — 62° , presumably identical with that described by Radcliff and Pollitt (A., 1921, i, 233) as being a polymorph of (I). This product is shown to be a mixture of m - $C_6H_4(NO_2)_2$ 35—50 and (I) 50—65%.

R. T.

Rearrangement of toluene derivatives by aluminium chloride. J. F. NORRIS and H. S. TURNER (J. Amer. Chem. Soc., 1939, 61, 2128—2131).— $AlCl_3 \cdot HCl$ at 50 — 100° causes rearrangement and disproportionation of o -, m -, and p - C_6H_4MeCl or p -cresol, but not of o -, m -, or p - $C_6H_4Me \cdot NO_2$ (at 100° ; tars formed at 150°) or p - $C_6H_4Me \cdot NMe_2$. The ratio of the products depends on the temp., time of heating, and amount of $AlCl_3$. With 0.1 mol. of $AlCl_3$ at 96° for 4.25 hr., the ease of rearrangement is o < m < p - C_6H_4MeCl . Thermal analysis of mixed isomerides, C_6H_4MeCl , is described.

R. S. C.

Use of n -butyl chlorosulphonate and chlorosulphite in the Friedel-Crafts reaction. C. BARKENBUS, R. L. HOPKINS, and J. F. ALLEN (J. Amer. Chem. Soc., 1939, 61, 2452—2453).—With $ClSO_2Bu^a$ (1 mol.) and $AlCl_3$ (2 mols.), at 0 — 5° , C_6H_6 (9 mols.) gives $CHPhMeEt$ (19), m - $C_6H_4(CHMeEt)_2$ (26.6), and $PhCl$ (11.2%); $PhMe$ gives m - (32.4) and p - $C_6H_4Me \cdot CHMeEt$ (19.6) with o - (21.8) and p - C_6H_4MeCl (6.2%) and products halogenated in the side-chain. Higher-boiling products are also formed. $ClSO_2Bu^a$, C_6H_6 , and $AlCl_3$ give $CHPhMeEt$ and S compounds.

R. S. C.

Ferric chloride as a condensing agent. W. M. POTTS and R. J. DODSON (J. Amer. Chem. Soc., 1939, 61, 2553).— $FeCl_3$ gives a better yield (82%) of $PhBu^a$ from C_6H_6 and Bu^aOH at room temp. than does $AlCl_3$, but causes only an indefinite reaction with $CHMeEt \cdot OH$ and none with Bu^aOH .

R. S. C.

Rearrangement of the xylenes by aluminium chloride. J. F. NORRIS and G. T. VAALA (J. Amer. Chem. Soc., 1939, 61, 2131—2134).—The ratio of the three isomerides obtained from each xylene by $AlCl_3$ depends on the temp. Rearrangement is accelerated by increase in the amount of $AlCl_3$, but not by HCl (increases decomp.) or $FeCl_3$.

R. S. C.

Chlorinations with sulphuryl chloride. I. Peroxide-catalysed chlorination of hydrocarbons. M. S. KHARASCH and H. C. BROWN (J. Amer. Chem. Soc., 1939, 61, 2142—2150).—Traces of org. peroxides enormously accelerate chlorination of many org. compounds by SO_2Cl_2 , making this a practical reagent. Yields are usually excellent and reaction times short. Boiling cyclohexane does not react with SO_2Cl_2 in the dark and only to the extent of 25% in 6 hr. in light; 0.001 mol. of Bz_2O_2 or (n - $C_{11}H_{23}CO_2$)₂ (I) causes complete reaction in 15—30 min. in the dark; animal C in rather large amount or $CuCl$ (0.2 mol.) is less effective, but S , I , PCl_5 , HCl , SO_2 , and O_2 are useless.

The products are chloro- and dichloro-*cyclohexanes*. $n\text{-C}_7\text{H}_{16}$ gives α - and *sec.*-chloroheptane. Pr^nCl gives $\text{CHMeCl}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_2(\text{CH}_2\text{Cl})_2$. Bu^nCl gives $\alpha\beta$ -, $\alpha\gamma$ -, and $\alpha\delta$ -dichlorobutane. $\text{CHMeCl}\cdot\text{CH}_2\text{Cl}$ gives $\text{CHMeCl}\cdot\text{CHCl}_2$, $\text{CMeCl}_2\cdot\text{CH}_2\text{Cl}$, and $\text{CHCl}(\text{CH}_2\text{Cl})_2$. $(\text{CH}_2\text{Cl})_2$ gives $\text{CHCl}_2\cdot\text{CH}_2\text{Cl}$. Pr^nBr gives $\text{CHMeCl}\cdot\text{CH}_2\text{Br}$, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, and products of higher b.p. $(\text{CHCl}_2)_2$ and CHCl_3 are unaffected. In general, CH_2 is more readily substituted than Me, and Cl depresses further substitution at the same C. PhMe similarly gives $\sim 100\%$ of CH_2PhCl or, with an excess of SO_2Cl_2 , CHPhCl_2 , but further substitution does not occur. $p\text{-C}_6\text{H}_4\text{MeCl}$ (gives $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$), PhEt (gives mainly CHPhMeCl), PhPr^s (gives mainly CPhMe_2Cl), PhBu^r (gives mainly $\text{CPhMe}_2\cdot\text{CH}_2\text{Cl}$), *m*-xylene [gives only $m\text{-C}_6\text{H}_4(\text{CH}_2\text{Cl})_2$], and CHPh_3 (gives CPh_3Cl), but not *o*- or *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, or CH_2Ph_2 , react similarly. Fluorene and $2\text{-C}_{10}\text{H}_7\text{Me}$ undergo nuclear chlorination. Sometimes use of a solvent (CH_2Cl_2 , CHCl_3 , CCl_4 , C_6H_6 , PhCl , or *o*- $\text{C}_6\text{H}_4\text{Cl}_2$) is advantageous, and the less stable (I) is preferable to Bz_2O_2 when reaction is slow. CH_2Ph_2 , a slow stream of O_2 , I, S, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$, SOCl_2 , PCl_3 , or *iso*- $\text{C}_5\text{H}_{11}\cdot\text{O}\cdot\text{NO}$ inhibits chlorination, e.g., of PhMe or *cyclohexane*, but AcCl , AcOH , and COPh_2 have no effect. Bz_2O_2 and SO_2Cl_2 at $70\text{--}80^\circ$ slowly give PhCl , SO_2 , and CO_2 . A chain mechanism for chlorination involving Cl atoms is suggested.

R. S. C.

Action of chlorine on thiocyanates. T. B. JOHNSON and I. B. DOUGLASS (J. Amer. Chem. Soc., 1939, 61, 2548—2550).— RSCN and aq. Cl_2 at 0° —room temp. give $\sim 75\%$ yields of RSO_2Cl [prep. when $\text{R} = \text{Me}$ or Et, described] and CNCl . $\text{CH}_2\text{Ph}\cdot\text{SCN}$ at $0\text{--}2^\circ$ gives CNCl and $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{H}$, converted in air into $(\text{CH}_2\text{Ph}\cdot\text{SO}\cdot)_2$ or by CH_2PhCl into $(\text{CH}_2\text{Ph})_2\text{SO}_2$; at $20\text{--}30^\circ$ it gives $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Cl}$, obtained also from $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{H}$ by aq. Cl_2 at $20\text{--}30^\circ$. $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HCl}$ gives only $\text{CH}_2\text{Ph}\cdot\text{SO}_2\text{Cl}$ (76%). Prep. of PhSO_2Cl from PhSCN is more difficult.

R. S. C.

Kinetics of sulphonation of nitrobenzene by sulphur trioxide.—See A., 1939, I, 570.

Derivatives of *o*- and *p*-nitrobenzenesulphinic acids.—See B., 1939, 1077.

Validity of the structure assigned to *cyclo*-octatetraene: pyrolysis of diquatary ammonium hydroxides related to Δ^4 - and Δ^2 -butene. C. D. HURD and L. R. DRAKE (J. Amer. Chem. Soc., 1939, 61, 1943—1945).—*Trimethyl-n-butylammonium bromide*, m.p. $197\text{--}198^\circ$ (sealed tube), is converted by Ag_2O in H_2O into the hydroxide, which, when heated, finally at 250° , in N_2 gives only Δ^4 -butene. $\alpha\beta$ -*Butylenedi(trimethylammonium bromide)* (prep. from $\text{CH}_2\text{EtBr}\cdot\text{CH}_2\text{Br}$ and NMe_3 at room temp.) gives similarly 44% of C_4H_6 (absorbed by alkaline KHgI_3) and 56% of $\text{CHMe}\cdot\text{C}\cdot\text{CH}_2$ (absorbed by 82% H_2SO_4). $\beta\gamma$ -*Butylenedi(trimethylammonium bromide)* [similarly prepared from $(\text{CHMeBr})_2$] gives 42—47% of $(\text{CH}_2\cdot\text{CH})_2$ (absorbed by molten maleic anhydride) and 58—53% of a mixture (absorbed by 82% H_2SO_4) of $(\text{CMe})_2$ and $\text{CHMe}\cdot\text{C}\cdot\text{CH}_2$. The structure of the *cyclo*octatetraene of Willstätter *et al.* (A., 1912, i, 17; 1913, i, 348) is thus uncertain, as it was deduced

from successive Hofmann degradations assumed to give only conjugated ethylenic linkings. R. S. C.

Synthesis of polyenes. I. Hexatriene and its polymerides. M. S. KHARASCH and E. STERNFELD (J. Amer. Chem. Soc., 1939, 61, 2318—2322).— NaNH_2 in liquid NH_3 causes smooth coupling of halides of weakly negative radicals, if the C carrying the halogen also carries H. Thus, addition of NaNH_2 (1 mol.) to $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$ (I) (1 mol.) gives 24—30% of $(\text{CH}_2\cdot\text{CH}\cdot\text{CH})_2$ (II), b.p. $76\text{--}78^\circ$, and 41—33% of 3-vinyl-4-butadienyl- Δ^1 -cyclohexene (III), b.p. $50\text{--}55^\circ/3$ mm. Addition of (I) (1.33 mols.) to NaNH_2 (2 mols.) gives 50% of (III) with some 4- β -2'-vinyl- Δ^3 -cyclohexenylvinyl-3-vinyl- Δ^1 -cyclohexene, b.p. $70\text{--}80^\circ/10^{-4}$ mm. [absorbs 5 H_2 in MeOH; does not react with $(\text{CH}\cdot\text{CO})_2\text{O}$ (IV)], and (?) 3-2'-vinyl- Δ^3 -cyclohexenyl-5- β -2''-vinyl- Δ^3 -cyclohexenylvinyl- Δ^1 -cyclohexene, b.p. $120\text{--}133^\circ/10^{-4}$ mm. [absorbs 6 H_2 in MeOH; does not react with (IV)]. Addition of NaNH_2 (2) to (I) (3 mols.) gives 50% of 4-chloromethyl-3-vinylcyclohexene, b.p. $44\text{--}48^\circ/8$ mm. [reduced (H_2 -PtO $_2$; 2.7 atm.) to 1-methyl-2-ethylcyclohexane], and less (II). The structure of (III) follows from its reaction with (IV) in C_6H_6 at $90\text{--}100^\circ$ to give an adduct, hydrolysed to the dicarboxylic acid, $\text{C}_{16}\text{H}_{20}\text{O}_4$, m.p. 178° , and from its hydrogenation (4 H_2) in MeOH to give 1-ethyl-2-n-butylcyclohexane, b.p. 268° , obtained also by interaction of 2-ethylcyclohexanone with MgBu^nBr , dehydration of the resulting carbinol by I, and finally hydrogenation (PtO $_2$) in AcOH at 2.5 atm.

R. S. C.

Addition of alkali metals to stilbenes. G. F. WRIGHT (J. Amer. Chem. Soc., 1939, 61, 2106—2110).—Contrary to Schlenk *et al.* (A., 1928, 1031), addition of Na, K, or Li to stilbene (I) or isostilbene gives a mixture of stereoisomerides. The reaction mechanism is discussed. Impure (I) is recovered (with one exception) from the reaction. Reaction is fastest in $(\text{CH}_2\cdot\text{OMe})_2$ (II) and good in Et_2O , but in C_6H_6 must be initiated by PhCl , and barely occurs in light petroleum (III) (b.p. $60\text{--}70^\circ$). The ratio of products depends on the solvent and on the characterising agent. With Li in Et_2O , CO_2 gives 55% of *meso*- and 26% of *dl*-($\text{CHPh}\cdot\text{CO}_2\text{H}$) $_2$ (IV); in (II) (Na or Li), only a trace of and, in C_6H_6 (Na or Li) or (III), no (IV) was isolated (purification is difficult) although the crude acid was a mixture. In (II) (Na), Me_2SO_4 gives 45% of $(\text{CHPhMe})_2$, b.p. $132\text{--}134^\circ/6$ mm., and 20% of the isomeride, m.p. 124° , the 4:4'-(NO_2) $_2$ -derivatives, m.p. 133° and 256° , respectively, of which with $\text{CrO}_3\text{--AcOH}$ give 90% of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$.

R. S. C.

Effect of substitution on the dissociation of hexa-arylethanes. VII. *m*- and *p*-Phenyl groups. C. S. MARVEL, M. B. MUELLER, and E. GINSBERG (J. Amer. Chem. Soc., 1939, 61, 2008—2010; cf. A., 1939, II, 103).— γ for 3.6% solutions in C_6H_6 at 25° indicates 11—12% of dissociation for $(m\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2)_2$ (I) and 13—14% for $(p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2)_2$ (10% in 7% solution). These figures and the known 60% dissociation of $\text{C}_2(\text{C}_6\text{H}_4\text{Ph}\cdot m)_6$ show that the *m*- are about as strongly dissociated as the *p*- $\text{C}_6\text{H}_4\text{Ph}$ derivatives, which does not accord with a relation of the stability of the free radicals with the

no. of possible resonance forms. Colour is no guide to the degree of dissociation. $m\text{-C}_6\text{H}_4\text{Ph}\cdot\text{MgBr}$ (prep. with aid of a little EtBr) and COPh_2 give $m\text{-phenyltriphenylcarbinol}$ (II), m.p. 104—105°, converted by $\text{HCl}\text{-CaCl}_2\text{-Et}_2\text{O}$ followed by EtOH into the *Et ether* (III), m.p. 78—79°. Hot, pure AcCl converts (II) or (III) into the *carbinyl chloride*, m.p. 86—87°, which with Ag gives (I) and thence by air $m\text{-phenyltriphenylmethyl peroxide}$, m.p. 164—165° R. S. C.

Cyclisation of dieninenes. VII. Dehydrogenation of *trans*-dodecahydrophenanthrene. *trans*-1-Keto-3:4-dialkyl-octahydronaphthalenes. C. S. MARVEL, R. MOZINGO, and E. C. KIRKPATRICK (J. Amer. Chem. Soc., 1939, 61, 2003—2008).—The structure of the *trans*- Δ^{11} -dodecahydrophenanthrene of Marvel *et al.* (A., 1936, 1101; 1938, II, 48) is confirmed. Its relative resistance to Se excludes a spiran structure; with Pd-C at 300—320° it gives only phenanthrene; H_2 -Raney Ni reduces the 9-CO of the parent ketone only at 185°/100—200 atm. (proof of steric hindrance), yielding mixed, waxy tetradecahydrophenanthrene-9-ols, b.p. 136—138°/2 mm. Formation of phenanthrene derivatives by Se -dehydrogenation of 1:2-dialkyl-naphthalene derivatives (cf. A., 1938, II, 48) is confirmed. Addition of 1-acetylenylcyclohexanol (prep. in 69% yield from cyclohexanone, C_2H_2 , and $\text{CMe}_2\text{Et}\cdot\text{OK}$ in $\text{CMe}_2\text{Et}\cdot\text{OH}\text{-Et}_2\text{O}$ at -15°), b.p. 77—78°/17 mm., followed by COMeBu^a , to MgEtBr in Et_2O gives 1- γ -hydroxy- γ -methyl- Δ^a -heptenylcyclohexanol, b.p. 124—126°/1 mm., dehydrated by KHSO_4 at 190—200° to 1- γ -methyl- n -hept- Δ^a -en- Δ^a -inenyl- Δ^1 -cyclohexene, b.p. 143—148°/21 mm., which with boiling 87% HCO_2H gives 38% of *trans*-1-keto-3-methyl-5- n -propyl-1:2:5:6:7:8:9:10-octahydronaphthalene (I), b.p. 107—108°/1 mm. (2:4-dinitrophenylhydrazine, m.p. 124—125°). Zn-Hg -18% HCl-AcOH reduction of (I) yields a mixture (II), $\text{C}_{14}\text{H}_{24}$, b.p. 115—120°/14 mm., containing some 6-methyl-5- n -propyl-1:2:3:4:7:8:9:10-octahydronaphthalene and 19% of a hydroazulene (absorption spectrum; Br-AcOH test of the mixture). With Se at 390—400°, (II) gives blue and mixed colourless compounds; the absorption spectrum of the mixture indicates presence of 35—40% of *trans*-*as*-octahydrophenanthrene. R. S. C.

Synthesis of phenanthrene derivatives. III. 9-Methylphenanthrene. C. K. BRADSHAW and R. W. H. TESS (J. Amer. Chem. Soc., 1939, 61, 2184—2185; cf. A., 1939, II, 362).—Cyclisation of $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{X}$ (A) by 2:1 AcOH -40% HBr gives the following yields of 9-methylphenanthrene: $\text{X} = \text{OMe}$ 50, OPh 32, $\text{O}\cdot\text{C}_{10}\text{H}_7\text{-}\beta$ 23, NEt_2 10, and Cl <1%, calc. on the ketone used. If $\text{X} = \text{OPh}$, AlCl_3 in CS_2 gives a 10% yield. Prep. of $\text{COMe}\cdot\text{CH}_2\cdot\text{OPh}$, b.p. 117—124°/19 mm., $\text{COMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_7\text{-}\beta$, m.p. 69—72°, and of (A) (from $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{MgI}$ and $\text{COMe}\cdot\text{CH}_2\text{X}$ except for $\text{X} = \text{OMe}$ which is obtained from MgMeI and $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OMe}$) is described. R. S. C.

Synthesis of 9:10-dialkyl-1:2-benzanthracenes. W. E. BACHMANN and J. M. CHEMERDA (J. Amer. Chem. Soc., 1939, 61, 2358—2361).—Conversion of 9:10-dimethoxy-9:10-dimethyl-9:10-di-

hydro-1:2-benzanthracene (I) into 9:10-dimethyl-1:2-benzanthracene (II) by Na (A., 1938, II, 270) involves formation of 9-sodio-10-methoxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene, followed by transannular loss of NaOMe , because (a) 1 mol. of the ether reacts with 2 Na , (b) the final product is present as hydrocarbon, (c) the reaction mixture remains almost colourless, (d) when (I) and (II) compete for Na , only (I) reacts, and (e) (II) is not obtained by interaction of its Na_2 derivative with (I). Some 9:10-dialkyl derivatives are prepared. 9:10-Diethoxy-9:10-dimethyl-9:10-dihydro-1:2-benzanthracene, m.p. 172—173·5°, is obtained from the 9:10-(OH) $_2$ -compound by $\text{H}_2\text{SO}_4\text{-EtOH}$ and with Na in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ gives 61% of (II); the Pr^a_2 , Pr^b_2 , and Bu^a_2 ethers could not be thus obtained. 9:10-Dimethoxy-9:10-di- n -propyl-9:10-dihydro-1:2-benzanthracene (similarly prepared), m.p. 176·5—177·5°, gives 95% of 9:10-di- n -propyl-1:2-benzanthracene, m.p. 100·5—101° (picrate, m.p. 107·5—108°). MgEtBr and 5-keto-5:6:7:8-tetrahydro-1:2-benzanthracene (III) give a carbinol, converted by Pd-C in N_2 at 310—320° into 5-ethyl-1:2-benzanthracene (IV) (65%), m.p. 118—119° (lit. 120°), and by KHSO_4 at 150—160° into 5-ethyl-7:8-dihydro-1:2-benzanthracene, m.p. 110—112°, which with Pd-C at 330—340° gives 70% of (IV). $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH at 70° oxidises (IV) to the quinone, which with MgMeI etc. affords 9:10-dihydroxy-, m.p. 201·5—204·5°, and 9:10-dimethoxy-9:10-dimethyl-5-ethyl-9:10-dihydro-1:2-benzanthracene, m.p. 197—200°, and 9:10-dimethyl-5-ethyl-1:2-benzanthracene (80%), m.p. 107—108°. Addition of $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Br}$ to (III) and Mg in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ gives 84% of 5-hydroxy-5-allyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 82—82·5°, converted by Pd-C-N_2 at 300° into 5- n -propyl-1:2-benzanthracene (V). MgPr^aBr and (III) in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ give impure 5-hydroxy-5- n -propyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 107—108·5°, which yields (V) by heating with HCO_2H and then with Pd-C . 5- n -Propyl-1:2-benzanthraquinone yields successively 9:10-dihydroxy-, m.p. 161·5—163°, and 9:10-dimethoxy-9:10-dimethyl-5- n -propyl-9:10-dihydro-1:2-benzanthracene, m.p. 157—159°, and 9:10-dimethyl-5- n -propyl-1:2-benzanthracene, m.p. 84—85°. 9:10-Dimethoxy-9:10-dimethyl-9:10-dihydro-1:2:5:6-dibenzanthracene (obtained from the diol by $\text{H}_2\text{SO}_4\text{-MeOH-C}_6\text{H}_6$), m.p. 310—320° (decomp.), and Na in $\text{Et}_2\text{O-C}_6\text{H}_6$ give 85% of 9:10-dimethyl-1:2:5:6-dibenzanthracene [*dipicrate*, m.p. 175°; *peroxide*, m.p. 206—207° (decomp.) or 218—219° (decomp.; preheated at 200°)]. R. S. C.

Synthetic experiments in the chrysene series. L. F. FIESER, L. M. JOSHEL, and A. M. SELIGMAN (J. Amer. Chem. Soc., 1939, 61, 2134—2139).—Addition of $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$ (prep. from $\text{CH}_2\text{Cl}\cdot\text{OMe}$ and CuCN in 81·6% yield), b.p. 120—120·6°, to 1- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$ in $\text{Et}_2\text{O-C}_6\text{H}_6$ gives $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{OMe}$ ketone, b.p. 144—146°/1 mm. (*semicarbazone*, m.p. 166·4—167·8°), which with MgMeCl affords α -methoxy- β -1-naphthylpropan- β -ol, m.p. 56·4—60·4°, b.p. 138—142°/1·5 mm., in 80% over-all yield (reversing the order of the Grignard reactions gives only a 12%

yield). KHSO_4 at 165–180° then gives α -1-naphthylpropaldehyde (I) (61%), b.p. 130–132°/2 mm. (semicarbazone, m.p. 203–204°), and its *enol Me ether* (16%), b.p. 120–122°/15 mm., hydrolysed by hot 20% HCl to (I). Fe powder and 1:1 $\text{AcOH-H}_2\text{O}$ reduce (I) to 1- $\text{C}_{10}\text{H}_7\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, b.p. 144–147°/3 mm. (3:5-dinitrobenzoate, m.p. 125.5–126.5°), which with most reagents gives impure halides, but with PCl_5 in C_6H_6 affords the *chloride*, b.p. 114–116°/1 mm. This probably has the normal structure, since the Grignard reagent (II) (obtained with difficulty) and solid CO_2 give 1- $\text{C}_{10}\text{H}_7\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Dehydration of the oily carbinol from (II) and 2-methylcyclohexanone gives ~25% of α -2-methyl- Δ^1 -cyclohexenyl- β -1-naphthylpropane, b.p. ~200–225°/2 mm. AlCl_3 in CS_2 at 0° then gives 1:6a-dimethyl-1:2:2a:3:4:5:6:6a-octahydrochrysene, b.p. ~220–240°/2 mm., which with Se at 320° yields 2-methylchrysene [$\text{s-C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 189.8–190.6°] (9%) by loss and migration of Me . Mg cyclohexyl chloride and (I) in Et_2O , first at <0° and then at room temp., give α -cyclohexyl- β -1-naphthyl-n-propyl alcohol, m.p. 59–61°, which with P_2O_5 at 150° or KHSO_4 at 160–180°, followed by AlCl_3 in CS_2 , gives an oil, converted by Se at 320° in very poor yields into a (?) methylchrysene, m.p. 90–100° [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 232–235° after sintering], and a (?) spiran [$\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 107–109°]. Mg 2-methylcyclohexyl chloride and (I) lead by similar reactions to an oil, which on dehydration gives small amounts of chrysene and another impure compound. $\text{o-C}_6\text{H}_4\text{Cl}\cdot\text{MgBr}$ and (I) give a carbinol, dehydrated by KHSO_4 to mixed isomeric α -o-chlorophenyl- β -1-naphthyl- Δ^1 -propenes, b.p. 150–180°/1 mm., which with KOH (fusion or in quinoline) gives tars. $\text{o-C}_6\text{H}_4\text{Br}\cdot\text{MgI}$ and (I) give an impure carbinol. M.p. are corr.

R. S. C.

Hydrobromides of 3:5-dihromo-o- and -p-toluidine and 5:6-dibromo-m-4-xylidine. A. WRÓBEL (Rocz. Chem., 1939, 19, 393–395).—The *hydrobromides*, m.p. 225° (decomp.), 221°, and 228° (decomp.), respectively, are decomposed by H_2O .

R. T.

Use of nitrobenzenesulphenyl chloride in identification of amines. J. H. BILLMAN and E. O'MAHONY (J. Amer. Chem. Soc., 1939, 61, 2340–2341).— $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\text{SOCl}$ and NH_3 or the appropriate amine in Et_2O or $\text{Et}_2\text{O-H}_2\text{O}$ give *o*-nitrobenzenesulphenamide, m.p. 124–125° (decomp.) [350° (decomp.)] (figures in parentheses or brackets are m.p. of the *hydrochlorides*), *o*-nitrobenzenesulphen-p-aniside, m.p. 138–138.5° [220° (decomp.)], -anilide, new m.p. 88.5–89° (198°), -p-bromoanilide, m.p. 146–146.5° [?] (decomp.), -p-chloroanilide, m.p. 143.5–144° [194° (decomp.)], -n-butyl-, m.p. 27–28° (142–142.5°), -cyclohexyl-, m.p. 51.5–52° (206–207°), -diethyl-, an oil (215–223°), -dimethyl-, m.p. 62.5–63° (171°), -ethyl-, m.p. 32.5–33° (108°), -methyl-, m.p. 35.5–36° (225–226°), and -n-propyl-, an oil (157–158°), β -, new m.p. 202–202.5° (254°), and - α -naphthyl-amide, m.p. 130.5–131° after softening at 125° [260° (decomp.)], -N-methylanilide, m.p. 86–86.5° (121–122°), -o-, m.p. 115.5–116° (215°), -m,

m.p. 106.5–107° (228°), and -p-toluidide, m.p. 136–136.5° (243°), from which the amines are regenerated in nearly 100% yield by $\text{HCl-Et}_2\text{O}$. M.p. are corr.

R. S. C.

Effect of temperature on the nitration of p-cymene. Synthesis of 6-nitrocarvacrylamine and certain derivatives. G. C. KYKER and R. W. BOST (J. Amer. Chem. Soc., 1939, 61, 2469–2470).—Nitration of *p*-cymene (best at –10° to –12°) to the 2:6-(NO_2)₂-derivative and reduction thereof by $(\text{NH}_4)_2\text{S}$ to 6-nitrocarvacrylamine, m.p. 52° (lit. 52°, 80–82°) (Ac derivative, m.p. 114–115°), is improved.

R. S. C.

New reaction of sulphonamides. *p*-Cresol-tyrosinase reagent. F. WYSS-CHODAT and R. FAILLARD (Arch. Sci. Phys. nat., 1939, [v], 21, Suppl., 50–53).—Sulphanilamide, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NMe}_2$, 2-*p*-aminobenzenesulphonamidopyridine, di-*p*-acetamidophenyl sulphone, and $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ give colours (varying shades of red) with *p*-cresol-tyrosinase, whereas $p\text{-CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and $\text{Na}_2 p\text{-}\alpha\text{-disulpho-}\gamma\text{-phenylpropylaminobenzenesulphonamide}$ do not.

J. L. D.

Schiff base hydrochlorides. Test for arylamines. J. V. SCUDI, H. D. RATISH, and J. G. M. BULLOWA (J. Amer. Chem. Soc., 1939, 61, 2554–2555).—A yellow colour, stable for several days but not to alkali, is produced by condensing arylamines of sulphanilamide type with, best, $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ in, best, H_2SO_4 -abs. EtOH . Halochromic salts of Schiff's bases are produced. *Cinnamylidene-sulphanilamide*, m.p. 213–215° (decomp.) [*hydrochloride*, m.p. 203–205° (decomp.)], and -*sulphapyridine*, m.p. 208–210° (decomp.) [*hydrochloride*, m.p. 178–180° (decomp.)], are described.

R. S. C.

Sulphanilamide derivatives. I. R. ADAMS, P. H. LONG, and A. J. JOHANSON. II. R. ADAMS, P. H. LONG, and A. JEANES (J. Amer. Chem. Soc., 1939, 61, 2342–2346, 2346–2349).—I. The following are prepared. Figures in parentheses are anti-streptococcal and -meningococcal activity, respectively, relative to $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2 = 4$, but the new compounds are generally less toxic. *p*-Propion-, new m.p. 226.5–227.5° (2, 3), *p*-n-butyr-, new m.p. 236–237° (1, 4), *p*-isobutyr-, new m.p. 248–249° (0–1, 4), and *p*-n-valer-amidobenzenesulphonamide, new m.p. 209–210° (3, –). *p*-Acetamidobenzenesulphon- β -hydroxyethylamide, m.p. 150–151° (0, 4), -di-(β -hydroxyethyl)amide, m.p. 158–159° (0, 1), - γ -, m.p. 133.5–135° (0, 1), and - β -hydroxy-n-propylamide, m.p. 166–167° (1, 0), - β -hydroxyisobutylamide, m.p. 185–187° (0–1, 2), - β - γ -dihydroxy-n-propylamide, m.p. 132–133° (0, 0), -N-methyl-N- β - γ -pentahydroxy-n-hexylamide, m.p. 87–91° (0, 0–1), -2'-hydroxycyclohexylamide, m.p. 218° (0, 0). *p*-Propionamidobenzenesulphon- β -hydroxy-n-propyl-, m.p. 148° (0, 3), and -isobutylamide, m.p. 172–172.5° (1, 3). *p*-n-Butyramidobenzenesulphon- β -hydroxyethyl-, m.p. 139° (0, 1), -di-(β -hydroxyethyl)-, m.p. 114–115° (0, 1), - β -hydroxy-n-propyl-, m.p. 127–128° (0, 2), and - β -hydroxyisobutylamide, m.p. 166° (0–1, 4). *p*-iso-Butyramidobenzenesulphon- β -hydroxy-ethyl-, m.p. 116.5° (2, 1), -n-propyl-, m.p. 144° (0–1, 3), and -isobutylamide, m.p. 173°

(0—1, 4). *p-n-Valeramidobenzenesulphon-β-hydroxy-n-propyl-*, m.p. 121.5° (0—1, 4), and *-isobutyl-amide*, m.p. 136—136.5° (0—1, 3). *p-iso-Valeramidobenzenesulphon-β-hydroxyisobutylamide*, m.p. 146—147° (0, 0). *p-Aminobenzenesulphon-β-hydroxyethyl-*, m.p. 95—97° (2, 3), *-di-(β-hydroxyethyl)*, m.p. 109—110° (2, 0—1), *-γ-*, m.p. 123—124° (0—1, 4), and *-β-hydroxy-n-propyl-*, m.p. 115—116° (1, 4), *-β-hydroxyisobutyl-*, m.p. 102—103° (0, 4), *-βγ-dihydroxy-n-propyl-*, m.p. 102—104° (0, 4), and *-2-hydroxycyclohexyl-amide*, m.p. 141—142° (0, 0). *p-Methylaminobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 90—91°. *p-Acetethylamide*, m.p. 134°. and *p-ethylamino-benzenesulphon-β-hydroxyisobutylamide*, m.p. 131.5° (0, —). *p-Benzylaminobenzenesulphon-β-hydroxyethylamide*, m.p. 115—116° (0—1, —). *p-Carboethoxyamidobenzenesulphon-amide*, m.p. 241—242° (1, 1), *-β-hydroxy-ethylamide*, m.p. 176° (1, 4), and *-n-propylamide*, m.p. 132° (0—1, 2), and *-morpholide*, m.p. 157—158° (0, 2). *p-Acetamido-*, m.p. 165—166° (1, 2), *p-propionamido-*, m.p. 189—190° (1, 1), *p-n-*, m.p. 191—193° (1, 2), and *p-iso-butylamide*, m.p. 147° (0—1, 0—1), and *p-amino-benzenesulphonmorpholide*, m.p. 217° (0—1, 0—1). *p-p'-Acetamido-*, m.p. 127—128° (0, 0), *p-p'-amino-*, m.p. 123—125° (0, 4), and *p-p'-carboethoxyamidobenzenesulphonamidobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 175—177° (0, 4). *p-p'-Acetamido-*, m.p. 213° (0, 0), and *p-p'-amino-benzenesulphonamidobenzenesulphon-β-hydroxyisobutylamide*, m.p. 184—185° (0—1, 4). *3-Acetamido-4-methoxybenzenesulphonamide*, m.p. 225.5° (0, 0—1), and *-β-hydroxy-ethyl-*, m.p. 152—153° (0, 0), *-n-propyl-*, m.p. 146—147° (0, 0), and *-isobutyl-amide*, m.p. 125° (0, 0—1). *3-Amino-4-methoxybenzenesulphonamide*, m.p. 142—142.5° (0, 0), and *-β-hydroxy-n-propylamide*, m.p. 102° (0, 0). *p-Propion-*, m.p. 113°, *-n-*, m.p. 120—121°, and *-isobutyl-*, m.p. 131—132°, *-n-*, m.p. 115—116°, and *-isovaler-*, m.p. 120—121°, *-acetmethyl-*, m.p. 136—137°, *-acetethyl-*, m.p. 142—143°, and *-carboethoxy-*, m.p. 103°. *-amidobenzenesulphonyl chlorides* are prepared from the appropriate anilide and ClSO_3H .

II. Succinyl (modified prep.) and ClSO_3H at 60—65° give a sulphonyl chloride, converted by 28% aq. NH_3 at 70° into *N-phenylsuccinamide-p-sulphonamide*, m.p. 234—238° (decomp.), or by the appropriate OH-amine (2 mols.) and 7% KOH (2.5 mols.) at 70° into *N-phenyl-N'-β-hydroxyethylsuccinamide-p-sulphon-β-hydroxyethylamide*, m.p. 137—142° (with less 5-anilo-2-pyrrolidone-4'-sulphon-β-hydroxyethylamide, m.p. 85—93°), and *p-β-carboxypropionamidobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 179—192° (decomp.) (*Et* ester, m.p. 125—128°). *p-OMe-CH₂-CO-NH-C₆H₄-SO₂Cl* and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ give *p-methoxyacetamidobenzenesulphon-β-hydroxyethylamide*, m.p. 125—127°. *OAc-CHMe-COCl* and *p-NH₂-C₆H₄-SO₂-NH₂* in Et_2O or *OAc-CHMe-CO-NHPh* and ClSO_3H (followed by aq. NH_3) give *p-α-acetoxy-*, m.p. 192.5°, and thence by 1.5*N*-NaOH at 50—55° *p-α-hydroxy-propionamidobenzenesulphonamide*, m.p. 196°. *p-α-Acetoxypropionamidobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 97—103°, is similarly obtained. Treating the appropriate dianilide with ClSO_3H , followed by the appropriate OH-amine, gives *malon-*, m.p. 203—208° (decomp.), *succin-*, m.p. 243—250° (decomp.), and *glutar-anilide-4:4'-di(sulphon-β-hydroxyethylamide)*, m.p. 196—198°, and *malon-*, m.p. 173—176° (decomp.), *succin-*, m.p. 265—270° (decomp.), and *glutar-anilide-4:4'-di(sulphon-β-hydroxy-n-propylamide)*, m.p. 187—190°. 2:5-Diketo-1:4-diphenylpiperazine similarly yields its 4':4''-*di(sulphon-amide)*, m.p. 325° (decomp.), *-β-hydroxyethylamide*, m.p. 260—270° (decomp.), and *-β-hydroxy-n-propylamide*, m.p. 280—284° (decomp.). *p-CH₂Cl-CO-NH-C₆H₄-SO₂Cl* and $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$ give *p-chloroacetamidobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 125—129°, converted by NH_4CNS in boiling EtOH into 2-anilo-4-ketotetrahydrothiazole-4'-sulphon-β-hydroxy-n-propylamide (I), m.p. 209—212°. *p-CHMeBr-CO-NH-C₆H₄-SO₂Cl* gives similarly *p-α-bromopropionamidobenzenesulphon-β-hydroxy-n-propylamide*, m.p. 140—143°, and thence the 5-Me derivative, m.p. 190—192°, of (I). *p-CH₂Cl-CO-NH-C₆H₄-SO₂·NH₂* and NH_4CNS yield (?) 3-phenyl-ψ-thiohydantoin-4'-sulphonamide [2-imino-3-anilo-4-ketotetrahydrothiophen-4'-sulphonamide], m.p. 258° (decomp.; darkens from 238°). These products have little or no antistreptococcal activity.

R. S. C.

Free radicals of the type of Wurster's salts. L. MICHAELIS, M. P. SCHUBERT, and S. GRANICK (J. Amer. Chem. Soc., 1939, 61, 1981—1992).—Stability of free radicals obtained by partial oxidation of *p*-diamines with Br in dil. solution [usually MeOH —0.005*N*-aq. AcOH (4:1)] at the optimum p_{H} (mostly ~3) is best judged by the rate of decomp. (as determined by colour changes and the nature of the electrometric titration curves), and is differentiated from effects due to the instability of the di-imines partly by being unaffected by increasing the concn. of the diamine. By 33 examples it is shown that stability is (a) decreased by Me *o*- to NHMe or NMe₂ (2 *o*-Me have enormous effect) or by OMe, Cl, or SO_3H in the ring, (b) increased by *N*-Me if there is no Me in the ring, and (c) unaffected by Me in the ring if the N are unmethylated (occasionally a slight decrease). Absorption spectra of the radicals are recorded. Results are explained as due to resonance of different forms of the radical.

R. S. C.

Reactivity of the aromatic nucleus. I. Karrer's theory of coupling. W. J. HICKINBOTTOM and E. W. LAMBERT (J.C.S., 1939, 1383—1386).—Karrer's observation (A., 1915, i, 1073) that $\text{NPh}(\text{C}_5\text{H}_{11}\text{-iso})_2$ (I) or NPhBu^t_2 in aq. AcOH with diazotised *p*-NH₂-C₆H₄-SO₃H (II) gives $\text{NHR}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ (R = Bu^t or iso-C₅H₁₁), with elimination of R, is not confirmed (cf. Reilly *et al.*, J.C.S., 1918, 113, 99); the product is $\text{NR}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$. The product from (I) and (II) (+ KOH) is *K* 4-diisoamylaminoazobenzene-4'-sulphonate, reduced by $\text{Na}_2\text{S}_2\text{O}_4$ to *p*-aminodisoamylaniline (dihydrochloride); *p*-benzamidodisoamylaniline, m.p. 101°. With *p*-NO₂-C₆H₄-N₂Cl (III), (I) gives 4'-nitro-4-diisoamylaminoazobenzene, m.p. 120°. $\text{NHPh}\cdot\text{C}_5\text{H}_{11}\text{-iso}$ (IV) and (II) give *K* 4'-isoamylaminoazobenzene-4'-sulphonate, reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to *p*-aminoisoamylaniline (dihydrochloride); (III) and (IV) give 4'-nitro-*N*-isoamylidiazaminobenzene, m.p. 72—73°. NPhBu^t_2 and (II) give *K* 4'-diisobutylaminoazobenzene-4-sulphonate, reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to

p-aminodiisobutylaniline [*dihydrochloride*, m.p. 223—224° (darkens ~210°); *p*-benzamidiisobutylaniline, m.p. 111°], also obtained by reducing the *hydrochloride* of *p*-nitrosodiisobutylaniline, m.p. 62—63°. NPhBu²₂ and (III) give 4'-nitro-4-diisobutylaminoazobenzene, m.p. 122—123°; 4'-nitro-4-methyl-tert.-butylaminoazobenzene, m.p. 133—134°; 4'-nitro-N-tert.-butyldiazaminobenzene, m.p. 142—143°; 4'-nitro-4-di-n-octylaminoazobenzene, m.p. 66—67°; 4'-nitro-N-n-octylaminodiazaminobenzene, m.p. 61—62°; 4'-nitro-4-dicetylaminoazobenzene, m.p. 70—71°, and 4-nitro-N-cetyldiazaminobenzene, m.p. 77°, are similarly prepared. *N*-Dialkylarylamines are purified through their picrates, which are less sol. than those of the corresponding *sec.* amines. The following are prepared: (I), b.p. 166—168°/18 mm. (*picrate*, m.p. 146°); NPhBu²₂, b.p. 142—144°/21 mm. (*picrate*, m.p. 141°); 1:4:2- and 1:3:2-C₆H₃Me₂·NMe₂, b.p. 82—82.5°/18 mm. (*picrate*, m.p. 154—155°); *o*-C₆H₄Cl·NMe₂, b.p. 101—103°/28 mm. (*picrate*, m.p. 133—134°). *Dicetylaniline*, m.p. 30°, is obtained from C₁₆H₃₃·NPh and C₁₆H₃₃I at 110°. E. W. W.

Effect of vitamin-C on enzymic oxidation of a monophenol. F. WYSS-CHODAT and F. CHODAT (*Arch. Sci. Phys. nat.*, 1939, [v], 21, Suppl., 53—58).—Tyrosinase and aq. *p*-cresol give first a yellow and then a brown solution, but not in presence of ascorbic acid (I), although the O₂ uptake is much increased with (I). (I) is without effect on the brown solution and inhibits the reaction between tyrosinase, *p*-cresol, and glycine. The extent of the O₂ uptake depends on the amount of (I) present and the rapidity of uptake on the amount of *p*-cresol. J. L. D.

Condensation products of phenols and ketones.

IV. *o*-Cresol and acetone. W. BAKER and D. M. BESLY (*J.C.S.*, 1939, 1421—1424).—The condensation product from *o*-cresol (I) and COMe₂ regarded by Niederl *et al.* (A., 1929, 551; cf. also A., 1932, 842) as CO(CH₂·CMe₂·C₆H₃Me·OH)₂ is identical with that regarded by Sükösd (*Acta Lit. Sci. Univ. Hung. Franc.-Joseph.*, 1932, 2, 230) as OH·C₆HMe(CMe₂)₃·C₆HMe·OH, and is 6:6'-*dihydroxy-3:3':5:3':3':5'-hexamethylbis-1:1'-spirohydrindene*, m.p. 245—246°. It is prepared (cf. Sükösd, *loc. cit.*) from (I), COMe₂, and conc. HCl at 100° (bath) for 60 hr. (purifying through the *diacetate*, m.p. 266—267°) and also from (4:3:1-OH·C₆H₃Me)₂·CMe₂ and AcOH—conc. HCl. It gives a *dibenzoate*, m.p. α-form, 170—171°, solidifying to β-form, m.p. 201°, *di-p*-nitrobenzoate, m.p. 247—248°, Me₂ ether, dimorphous, m.p. 158—159°, and 7:7'-Br₂-derivative, m.p. 224°, is oxidised (KMnO₄—AcOH) to give some phoronic anhydride, and nitrated (hot conc. HNO₃—AcOH) to NO₂-compounds, m.p. 233—234° (decomp.), and ~225°, which are probably degradation products. E. W. W.

Reaction of *p*-fluorophenol with benzene and aluminium chloride. A. W. WESTON and C. M. SUTER (*J. Amer. Chem. Soc.*, 1939, 61, 2556—2557).—The by-product formed during de-ethylation of *p*-C₆H₄F·OEt by AlCl₃ in C₆H₆ (A., 1939, II, 109) is *p*-C₆H₄Ph·OH and is obtained also from *p*-C₆H₄F·OH, C₆H₆, and AlCl₃. *p*-C₆H₄Cl·OH does not react with

C₆H₆—AlCl₃, nor does *p*-C₆H₄F·OH with PhMe or PhCl. R. S. C.

Synthesis of 2-*n*-butyl-α-naphthol. Y. F. CHI (*J. Amer. Chem. Soc.*, 1939, 61, 2487—2488).—α-C₁₀H₇·OH, PrⁿCO₂H, and ZnCl₂ give 2-*n*-butyryl-α-naphthol, m.p. 85—86°, b.p. 145—152°/1 mm. (*oxime*, m.p. 119°; *semicarbazone*, m.p. 201—202°; Me, m.p. 80—81°, b.p. 155—157°/1 mm., and Et ether, m.p. 79—81°, b.p. 158—159°/1 mm.) (with some α-C₁₀H₇·*n*-butyrate, m.p. 95.5—96.5°, b.p. 125—130°/1 mm.), reduced by Zn—Hg—HCl to 2-*n*-butyl-α-naphthol, m.p. 73—74°, b.p. 140—149°/1 mm. R. S. C.

Structure of fluorene. W. C. LOTHROP (*J. Amer. Chem. Soc.*, 1939, 61, 2115—2119).—Pyrolysis of allyloxyfluorene derivatives indicates that little or no fixation of the ethylenic linkings occurs, other reactions notwithstanding. Fluorene is considered to be benzenoid rather than naphthoid. 2-Hydroxyfluorene, CH₂:CH·CH₂Br, and anhyd. K₂CO₃ in boiling COMe₂ give 2-allyloxyfluorene (99%), m.p. 95—96°, which at 235—238° gives a mixture, separable with difficulty into 2-hydroxy-3- (~60%), m.p. 87—88°, and 1-allylfluorene (~25%), m.p. 111—112°. These products give allyl ethers, m.p. 44—45° and 82—83°, respectively, pyrolysis of which yields in both cases 2-hydroxy-1:3-diallylfluorene, m.p. 58°, b.p. 170°/3 mm. Crude 3-methoxyfluorene-9-one, red P, and HI in boiling AcOH give 3-hydroxyfluorene, m.p. 136—137° (*benzoate*, m.p. 128°), the allyl ether of which gives a gum when pyrolysed. *o*-COCl·C₆H₄·NH·SO₂·C₆H₄Me-*p*, 1:4:2-C₆H₃Me₂·OMe, and AlCl₃ in CS₂ give 2'-*p*-toluenesulphonamido-4-methoxy-2:5-dimethylbenzophenone, m.p. 140—141° (*N*-Me derivative, m.p. 168—169°, prepared by Me₂SO₄—alkali), slowly hydrolysed by conc. H₂SO₄ at room temp. to the *NH₂-ketone*, m.p. 102—104°. Diazotisation etc. then gives (84% yield under stated conditions) 3-methoxy-1:4-dimethylfluorenone (I), m.p. 140—141°, and a little 2'-hydroxy-4-methoxy-2:5-dimethylbenzophenone, m.p. 94—95° (*acetate*, m.p. 81—82). HI—red P—AcOH converts (I) into 3-hydroxy-1:4-dimethylfluorene (II), m.p. 180—181° (*acetate*, m.p. 100°; 2-benzeneazo-derivative, m.p. 183—184°), or (shorter heating) 3-hydroxy-1:4-dimethylfluorenone, m.p. 223—224° (*acetate*, m.p. 133—134°), obtained also by 48% HBr. The allyl ether, m.p. 54—55°, of (II) when heated at 215° in N₂ gives 3-hydroxy-1:4-dimethyl-2-allylfluorene, m.p. 150—151°. Improved prep. from *m*-cresol (118 g.) gives 1:2:3-C₆H₃Me₂·OMe (26.3 g.) (by way of 2:1:3-NH₂·C₆H₃Me·OMe and 1:2:3-C₆H₃MeBr·OMe), which by methods given above affords 2'-*p*-toluenesulphonamido-, m.p. 136—138°, 2'-*p*-toluenesulphonmethylamido-, m.p. 160°, 2'-amino-, m.p. 144—145°, and 2'-hydroxy-4-methoxy-2:3-dimethylbenzophenone, m.p. 135—136° (*acetate*, m.p. 97—98°), 3-methoxy-, m.p. 178—179°, and 3-hydroxy-1:2-dimethylfluorenone, m.p. 258—259° (decomp.) (*acetate*, m.p. 137—138°), 3-hydroxy-1:2-dimethylfluorene, m.p. 212—213° (decomp.) [*acetate*, m.p. 146—147°; *benzeneazo*-derivative, m.p. 201° (decomp.); allyl ether, m.p. 102—103°], and 3-hydroxy-1:2-dimethyl-4-allylfluorene, m.p. 135—136°. R. S. C.

Isomeric $\gamma\delta$ -di-*p*-hydroxyphenyl- Δ^8 -*n*-hexenes. F. VON WESSELY and A. KLEEDORFER (Naturwiss., 1939, 27, 567—568; cf. A., 1939, II, 259, 312).—Dehydration of $\gamma\delta$ -di-*p*-anisyl-*n*-hexan- γ -ol gives *trans*-(I) and impure *cis*-(*p*-OMe·C₆H₄·CEt)₂ and isomeric $\gamma\delta$ -di-*p*-anisyl- Δ^8 -*n*-hexenes, m.p. 50° (II) and an oil (III). From (II) and (III) are obtained $\gamma\delta$ -di-*p*-hydroxyphenyl- Δ^8 -*n*-hexenes, m.p. 153° (IV) (*diacetate*, an oil; *dibenzoate*, m.p. 126°), and m.p. 143.5° (V) (*diacetate*, m.p. 74°; *dibenzoate*, m.p. 184°), respectively. (II) and (III) are converted by O₃ into ethyldeoxyanisoin, by I into (I), and by H₂-Pd into (*p*-OMe·C₆H₄·CHEt)₂, m.p. 146°. Estrogenic activity is (*p*-OH·C₆H₄·CHEt)₂, m.p. 186° > (IV) > (*p*-OH·C₆H₄·CHEt)₂, m.p. 130° (prep. by hydrogenation of diethylstilboestrol) > (V). R. S. C.

Stereochemistry of diphenyls. XLVII. 2:5-Di-*m*-4'-xylylquinols and their derivatives. R. ADAMS and G. C. FINGER (J. Amer. Chem. Soc., 1939, 61, 2182—2183; cf. A., 1939, II, 505).—Prep. of 2:5-di-*m*-4'-xylylquinol and its 3:6-Br₂-derivatives is modified and the yields are recalcd. (cf. Browning *et al.*, A., 1930, 1588). Addition of 3:6-dibromo-2:5-di-*m*-4'-xylylbenzoquinone in EtOH to aq. NaOH at room temp. gives 3:6-dihydroxy-2:5-di-*m*-4'-xylylbenzoquinone (I), m.p. 282—284°, the *diacetate* (prepared by hot Ac₂O-C₅H₅N), m.p. 186—188°, of which is hydrolysed by HCl-AcOH to (I) and reduced by SnCl₂-EtOH to 3:6-diacetoxy-2:5-di-*m*-4'-xylylquinol, m.p. 213—215°. Acetylation, best by hot Ac₂O-C₅H₅N and a trace of SnCl₂, then yields 1:2:4:5-tetra-acetoxy-3:6-di-*m*-4'-xylylbenzene, m.p. 276—278°. In no case were diastereoisomeric forms obtained. R. S. C.

Synthesis of 6:7-dihydroxy-1:4-dimethylphenanthrene from *p*-xylylacetic acid and 6-nitroveratraldehyde by the Pschorr reaction. J. T. CASSADAY and M. T. BOGERT (J. Amer. Chem. Soc., 1939, 61, 2461—2463).—6:3:4:1-NO₂·C₆H₂(OMe)₂·CHO (improved prep.), m.p. 132—133° (lit. 133.5—134.5°), and 1:4:2-C₆H₃Me₂·CH₂·CO₂H in Ac₂O at 105—110° give 6-nitro-3:4-dimethoxy- α -*p*-2'-xylylcinnamic acid, m.p. 226—227°, reduced by FeSO₄-aq. NH₃ to the 6-NH₂-acid, m.p. 191—192°, which with *iso*-C₅H₁₁·O·NO and H₂SO₄ in dioxan, followed by NaH₂PO₄ and Cu powder, gives 6:7-dimethoxy-1:4-dimethylphenanthrene-10-carboxylic acid (I), m.p. 215.5—216.5°. Boiling with basic Cu carbonate in quinaldine then gives 6:7-dimethoxy-, m.p. 175—176°, and thence (48% HBr) 6:7-dihydroxy-1:4-dimethylphenanthrene (35%), m.p. 164—164.5° (*diacetate*, m.p. 133—133.5°) [also obtained less well (10—15%) from (I) by HBr-AcOH], sol. in cold olive oil and appreciably sol. in H₂O. M.p. are corr. R. S. C.

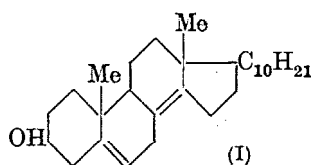
Synthesis of vitamin-A methyl ether. F. B. KIPPING and F. WILD (Chem. and Ind., 1939, 802).—COMe·[CH₂]₂·OMe is converted by CH₂:CH·CH₂MgCl into the carbinol, dehydrated to ζ -methoxy- δ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene, which with Br followed by KOH affords α -bromo- ζ -methoxy- δ -methyl- $\Delta^{\beta\delta}$ -hexadiene. The Li derivative therefrom with β -ionone gives a *tert*-alcohol dehydrated to vitamin-A Me ether. No details are given. R. S. C.

Organic peroxides. VI. Cyclane peroxides. N. A. MILAS, S. A. HARRIS, and P. C. PANAGIOTAKOS (J. Amer. Chem. Soc., 1939, 61, 2430—2432; cf. A., 1938, II, 469).—cyclopentanone (I) and 0.6M-H₂O₂-Et₂O give 1-hydroxycyclopentyl *H* peroxide (II) or di-(1-hydroxycyclopentyl) peroxide (III), oils. When kept, (II) gives its solvate, +0.5H₂O₂, m.p. 73—75° (gas at 105°), also obtained from (I) by 30% H₂O₂ and converted in hot Et₂O or 1:1 Et₂O-light petroleum into dicyclopentylidene peroxide, ([CH₂]₄C<O, m.p. 160° (decomp.). When kept,

(III) gives an insol. polymeride, ([CH₂]₄C<O)_x, m.p. 166° (decomp.). Similarly are prepared 1-hydroxy-cyclohexyl, m.p. 76—78°, -3- (also +0.5H₂O₂, m.p. 120—121°), -2-, and -4-methylcyclohexyl *H* peroxide, oils, di-(1-hydroxycyclohexyl), m.p. 68—70° di-(1-hydroxy-3-, -2-, and -4-methylcyclohexyl), and di-(1-hydroxycyclooctyl) peroxide, oils, and 1-hydroxy-cyclo-heptyl, m.p. 92—94°, and -octyl *H* peroxide, an oil. R. S. C.

$\alpha\beta$ -Diarylacetylene glycols. II. An enediol from hexaethylbenzil. R. C. FUSON, J. CORSE, and C. H. MCKEEVER (J. Amer. Chem. Soc., 1939, 61, 2010—2012; cf. A., 1939, II, 260).—2:4:6-C₆H₂Et₃·COCl (prep. in 85% yield from the acid by SOCl₂ or less well by PCl₅), b.p. 108—110°/2 mm., with Mg + MgI₂ in Et₂O-C₆H₆-N₂ gives $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-2:4:6-triethylphenylethyne (I), m.p. 149—151° (decomp.; in air, 154—155.5° (in N₂), (2:4:6-C₆H₂Et₃·CO)₂ (II), and some 2:4:6-C₆H₂Et₃·CO₂H. (I) is stable in air, insol. in 40% aq. NaOH, reduces Tollens' reagent, FeCl₃, and Cu(OAc)₂ at 0°, gives a positive 2:6-dichlorobenzene-iodophenol test, and is oxidised to (II). Catalytic hydrogenation of (II) in Ac₂O yields a *cis*-*diacetate*, m.p. 133.5—134°, of (I); a *trans*-*diacetate*, m.p. 188—190°, is obtained from (I) by boiling Ac₂O. BzCl-C₅H₅N converts (I) into *dibenzoates*, m.p. 235—236° and 124—124.5°. Hot HCl-MeOH converts (I) into 2:4:6:2':4':6'-hexaethylbenzoin, m.p. 64—65.5°, but the compounds are not interconvertible. The non-acidity of (I) indicates that C:C-OH is acidic only if a neighbouring group is negative (e.g., CO); absorption max. at 2.78 and 2.83 μ . are characteristic of acidic OH. R. S. C.

Sitosterol complex. Structure of α_1 -sitosterol. S. BERNSTEIN and E. S. WALLIS (J. Amer. Chem. Soc., 1939, 61, 2308—2313).— α_1 -Sitosterol is probably (I), in which the OH is *cis* to the Me on C₁₀. The absorption spectrum and failure of α_1 -sitosteryl acetate (II)



(prep. by Ac₂O at 100°), m.p. 137—138°, to react with maleic anhydride indicate non-conjugation of the ethylenic linkings. H₂-PtO₂ in AcOH at room temp. or 60° reduces (II) (by 5:6-addition) to α_1 -dihydrositosteryl acetate (III), m.p. 108.5—110.5°, [α]_D²⁵ +35.1° in CHCl₃ (hydrolysed by 5% KOH-EtOH to α_1 -dihydrositosterol, m.p. 152—154°, [α]_D²⁵ +10.9° in CHCl₃), but in presence of a little conc. HCl at

65—70° gives α_1 -sitostanyl acetate (IV), m.p. 147—148°, $[\alpha]_D^{25} + 39.4^\circ$ in CHCl_3 , hydrolysed to α_1 -sitostanol, m.p. 185—186°, $[\alpha]_D^{25} + 27.0^\circ$ in CHCl_3 . Dry HCl-CHCl_3 at 0° converts (III) (by migration of the double linking from 8:14 to 14:15) into α_1 -isodihydrositosteryl acetate (V), m.p. 137.5—138.5°, $[\alpha]_D^{25} + 42.0^\circ$ in CHCl_3 , hydrolysed to α_1 -isodihydrositosterol, m.p. 152—154°, $[\alpha]_D^{25} + 31.0^\circ$ in CHCl_3 , and hydrogenated in AcOH to (IV). With BzO_2H in CHCl_3 , (V) gives the 14:15-oxide, m.p. 152—154°, converted by a little H_2SO_4 in AcOH at 100° into $\Delta^8,9,14:15$ -sitostadienyl acetate, m.p. 121.5—122°.

R. S. C.

α_3 -Sitosterol, $\text{C}_{29}\text{H}_{48}\text{O}$, m.p. 142°, $[\alpha]_D^{25} + 1.65^\circ$ in CHCl_3 , and its benzoate, m.p. 167.5—168°, $[\alpha]_D^{25} + 14.85^\circ$ in CHCl_3 , and *m*-dinitrobenzoate, m.p. 202.5—203°, $[\alpha]_D^{25} + 15.35^\circ$ in CHCl_3 .—See A., 1939, III, 950.

Sugar-cane wax. IV. Diol derivatives of sugar-cane sitosterol and stigmasterol. V. Oxidation of sugar-cane sitostanyl acetate. T. MITUI (J. Agric. Chem. Soc. Japan, 1939, 15, 795—804, 805—808).—IV. Sugar-cane sitosterol (I) is probably identical with 22-dihydrostigmasterol and contains the side-chain $\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHEtPr}^6$ (cf. A., 1938, II, 232). The syntheses of sitostane-3:6-, m.p. 215°, and -3:7-diol, m.p. 176°, and stigmastane-3:6-, m.p. 213°, and -3:7-diol, m.p. 174°, from (I) and stigmasterol are described; α -saccharostanediol (A., 1939, II, 421) differs from these and the 3:4-diols.

V. Oxidation of sugar-cane sitostanyl acetate with CrO_3 gives *trans*-androsterone, 3-hydroxynorallocholic acid, and 3-hydroxyætiollobilanic acid [Me_2 ester, m.p. 78° (sinters at 74°)]. J. N. A.

Constitution of cholesterol. XVI. Oxidation by peracetic acid. F. PIRRONE and R. VANNUCCI (Gazzetta, 1939, 69, 470—478).—A dil. solution of cholesterol in aq. H_2O_2 - AcOH gives (a) in sunlight, the diacetate of cholestane-3:5:6-triol (I) (cf. Dunn *et al.*, A., 1934, 1347); (b) at the b.p., (I) and a substance, $\text{C}_{27}\text{H}_{46}\text{O}_4$ (II), m.p. 115—116° (turbid, clear at 121—122°); (c) at 100° (bath), traces of (II) and of a substance, m.p. 63—65°. E. W. W.

Alepric, aleprylic, aleprestic, and aleprolic acids, new homologues of chaulmoogric acid. H. I. COLE and H. T. CARDOSO (J. Amer. Chem. Soc., 1939, 61, 2349—2351).—Alepric, $\text{C}_{14}\text{H}_{24}\text{O}_2$, m.p. 48°, $[\alpha]_D^{25} + 77.12^\circ$ (*Et* ester, b.p. 174°/10 mm., $[\alpha]_D^{25} + 66.54^\circ$), aleprylic, $\text{C}_{12}\text{H}_{20}\text{O}_2$, m.p. 32°, $[\alpha]_D^{25} + 90.78^\circ$ (*Et* ester, b.p. 148°/10 mm., $[\alpha]_D^{25} + 79.14^\circ$), aleprestic (70.5% pure), $\text{C}_{10}\text{H}_{16}\text{O}_2$ [*Et* ester, b.p. (calc.) 122°/10 mm.], and aleprolic acid (42% pure), $\text{C}_8\text{H}_{14}\text{O}_2$ [*Et* ester, b.p. (calc.) 70°/10 mm.], are isolated as previously described (A., 1939, II, 318). An optically inactive, monounsaturated and a saturated ester are probably also present in *Hydnocarpus wightiana* oil.

R. S. C.

Arylation of oils and fats. II. Crystalline derivatives of phenylstearic acid. Syntheses of the *S*-benzylthiuronium salt, *p*-substituted phenacyl esters, and *p*-xenylamide of phenylstearic acid. W. KIMURA and H. TANGUCHI (J. Soc. Chem. Ind. Japan, 1939, 42, 234—235b).—1-Phenyl-

stearic acid (I) is converted into the *S*-benzylthiuronium salt (II), m.p. 134—135°, *p*-xenylamide (III), m.p. 91—92°, *p*-iodophenacyl, m.p. 34—35°, and *p*-phenylphenacyl (crude), m.p. ~35—40°, ester; 2-*i*-phenylheptadecylbenziminazole is an oil. (II) and particularly (III) are suitable for the identification of (I). H. W.

Relation between chemical constitution and local anaesthetic activity. III. Substituted cinnamic esters of dialkylamino-alcohols. IV. Local anaesthetics containing an ephedrine-like nucleus. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1939, 28, 499—502, 502—506).—III. α - and β -Alkylcinnamic acids (prepared by Claisen condensation and Reformatsky synthesis, respectively) are converted through the chlorides or Na salts into the following ester hydrochlorides: β -diethylaminoethyl α -methyl-, m.p. 133—134.5°, α -ethyl-, m.p. 145°, α -*n*-propyl-, m.p. 125—126°, α -isopropyl-, m.p. 152—153°, α -*n*-butyl-, m.p. 105.5—106.5°, α -*n*-amyl-, m.p. 83—85°, and γ -diethylamino-propyl α -ethyl-cinnamate hydrochloride, m.p. 143.8—144.4°; β -diethylaminoethyl *o*-chloro-, m.p. 127.5—128°, and *p*-dimethylamino- α -ethylcinnamate hydrochloride, m.p. 170—171°; γ -diethylaminopropyl *p*-, m.p. 191—192°, and *o*-amino- α -ethylcinnamate dihydrochloride, m.p. 170—170.5°; β -diethylaminoethyl β -methyl-, m.p. 141—142°, and β -propyl-cinnamate hydrochloride. $\text{CHPh}\cdot\text{Calk}\cdot\text{COCl}$ and $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NMe}_2$ in an inert solvent give *N*-(β -diethylaminoethyl)- α -methyl-, m.p. 111—112.5°, α -ethyl-, m.p. 163—164°, α -*n*-propyl-, m.p. 134.2—134.9°, α -*n*-butyl-, m.p. 124.5°, and α -amyl-cinnamamide hydrochloride, m.p. 92—95°. All the compounds possess pronounced local anaesthetic activity.

IV. The following substances were prepared (cf. Cherbuliez *et al.*, A., 1931, 350); all possessed local anaesthetic, but no significant vasopressor, activity: β -diethylamino- γ -hydroxy- γ -phenylpropyl benzoate, m.p. 181—181.5°, α -ethylcinnamate, m.p. 149—150°, phenylcarbamate, m.p. 203—204°, and *p*-ethoxybenzoate, m.p. 177—178°, hydrochloride; β -diethylamino- γ -methoxy- γ -phenylpropyl phenylcarbamate hydrochloride, m.p. 198—199.5°; β -dimethylamino- γ -hydroxy- γ -phenylpropyl benzoate hydrochloride, m.p. 215—216°. F. O. H.

Synthesis of *dl*- β -cyclohexylalanine. D. SHEMIN and R. M. HERBST (J. Amer. Chem. Soc., 1939, 61, 2471—2472).—In presence of freshly prepared PtO_2 , H_2 reduces $\text{CHPh}\cdot\text{C}(\text{NHAc})\cdot\text{CO}_2\text{H}$ in AcOH to *N*-acetyl- β -*dl*-cyclohexylalanine, m.p. 178°, hydrolysed by HCl to *dl*- β -cyclohexylalanine, *cryst.* (*Bz* derivative, m.p. 182—182.5°), which with PhNCO yields α -phenylcarbamido- β -cyclohexylpropionic acid, m.p. 177.5° (decomp.), and thence (HCl-EtOH) 3-phenyl-5-cyclohexylmethylhydantoin, m.p. 172.5°. M.p. are corr. R. S. C.

α -Naphthacetyl amino-acids.—See B., 1939, 1025.

Analogue of thyroxine. M. BOVARNICK, K. BLOCH, and G. L. FOSTER (J. Amer. Chem. Soc., 1939, 61, 2472—2474).—3:5-Di-iodo-4-*p*-anisyl oxybenzenediazonium chloride in $\text{AcOH-H}_2\text{O-H}_2\text{SO}_4$ at 100—110° gives 3:5-di-iodo-4-hydroxyphenyl *p*-anisyl ether, m.p. 160—163°, converted by 3:4:5:1-

$C_6H_2I_3NO_2$ and anhyd. K_2CO_3 in boiling COMeEt into 2:6:3':5'-tetraiodo-4-nitro-4'-p-anisilyoxydiphenyl ether, m.p. 190—192°, reduced by $SnCl_2 \cdot HCl \cdot AcOH$ to the 4- NH_2 -ether, m.p. 185—187° (hydrochloride, unstable). The diazonium compound (prep. by OEt.NO in AcOH) therefrom with $KCu(CN)_2$ gives 2:6:3':5'-tetraiodo-4'-cyano-4'-p-anisilyoxydiphenyl ether, m.p. 225—226°, converted by $HCl-SnCl_2-Et_2O-CHCl_3$ into the 4-aldehyde, m.p. 196—198°. With $NHAc \cdot CH_2CO_2H$ and $NaOAc$ in boiling Ac_2O this gives α -acetamido- β -3:5:3':5'-tetraiodo-4'-p'-anisilyoxy-p-phenoxyphenylacrylic azlactone, m.p. 264—265°, which is reduced by red P-HI- Ac_2O to β -3:5:3':5'-tetraiodo-4'-p'-hydroxyphenoxy-p-phenoxyphenylalanine [thyroxine p-hydroxyphenyl ether] (I), m.p. 267—268° (decomp.), converted by I in $NH_3-MeOH-H_2O$ into the 3:5:3':5':3'':5''-I₆-compound (II), decomp. from 210°. (I) and (II) are physiologically inactive. R. S. C.

Mohler's test for benzoic acid. E. T. ILLING (Analyst, 1939, 64, 586; cf. A., 1932, 632).—The rapid fading of the colour due to $C_6H_5(NH_2)_2 \cdot CO_2H$ is prevented by diluting with a solution obtained by successive treatment of aq. $H_2SO_4-KNO_3$ with aq. NH_3 and aq. $NH_2OH \cdot HCl$. E. C. S.

Preparation of 5-fluoroacetylsalicylic acid. C. M. SUTER and A. W. WESTON (J. Amer. Chem. Soc., 1939, 61, 2317—2318).—2:5:1-OEt- $C_6H_3F \cdot MgBr$ (prep. with aid of EtBr) and CO_2 in Et_2O give 5-fluoro-2-ethoxybenzoic acid, m.p. 65.5—66.5°, hydrolysed by HI (d 1.7) to 5-fluorosalicylic acid, m.p. 178.5—179.5°. The F increases the toxicity to mice of this and its O-Ac derivative, m.p. 130—131°. R. S. C.

Stereochemistry of diphenyls. XLVI. 2-Substituted diphenyls. R. ADAMS and T. L. CAIRNS (J. Amer. Chem. Soc., 1939, 61, 2179—2181; cf. A., 1938, II, 337).—o- $C_6H_4Br \cdot NO_2$, m- $C_6H_4I \cdot CO_2Et$, and activated Cu-bronze, first at 215° and then at 235—250°, give an ester, hydrolysed to 2-nitrodiphenyl-3'-carboxylic acid, m.p. 207—208°, the Et ester (prepared by $SOCl_2$ and then EtOH), m.p. 63—65°, b.p. 215°/11 mm., of which in 95% EtOH is boiled with Raney Ni and then reduced by H_2-PtO_2 at 3—3.5 atm., yielding Et 2-aminodiphenyl-3'-carboxylate (I), m.p. 75—76°. A diazo-reaction then affords 2-iododiphenyl-3'-carboxylic acid, m.p. 168—170°, which gives a homogeneous quinine salt, m.p. 184—187°, $[\alpha]_D^{25} -106^\circ$ in MeOH. The Ac derivative, m.p. 111—111.5°, of (I) with Na and Me_2SO_4 in C_6H_6 gives homogeneous 2-acetmethylamido- (II), m.p. 228—239°, and a little 2-acetamido-diphenyl-3'-carboxylic acid, m.p. 183—188°. Resolution of (II) failed; quinine salts, m.p. 173—182°, $[\alpha]_D^{25} -129^\circ$, and m.p. 172.5—173.5°, $[\alpha]_D^{25} -140^\circ$ in $CHCl_3$, were obtained, but did not mutarotate and gave the same inactive acid. M.p. are corr. R. S. C.

2:3-Hydroxynaphthoic acid.—See B., 1939, 1021.

Relation between resonance-stabilised chelate rings and acidity. R. T. ARNOLD and J. SPRUNG (J. Amer. Chem. Soc., 1939, 61, 2475—2476; cf. A., 1938, II, 280).—Among cyano-, aldehydo-, and nitro-

naphthols and some analogous C_6H_6 derivatives, "fixation" of the ethylenic linkings leads to increasing stability of the chelate rings and thus decreasing acidity. 2:1-CN- $C_{10}H_6 \cdot SO_3Na$ and KOH in glycerol at 140° give 2-cyano- α -naphthol, m.p. 178—179° (acetate, m.p. 87°). 4:1-OAc- $C_{10}H_6 \cdot CHO$ (prep. from the OH-aldehyde by $NaOAc \cdot Ac_2O \cdot AcOH$), m.p. 103—105°, $NH_2OH \cdot HCl$, $NaOAc$, and $NaHCO_3$ in boiling, aq. MeOH give 4-hydroxy-1-naphthaldozime, decomp. 150°, the N-Ac derivative, decomp. 155°, of which with C_5H_5N in hot EtOH gives 4-cyano- α -naphthol, m.p. 176—176.5°, also obtained from 4:1-CN- $C_{10}H_6 \cdot N_2 \cdot BF_4$. R. S. C.

Hydrolysis of arylamides used as dye intermediates. I. V. HOPPER, J. H. MACGREGOR, and F. J. WILSON (J. Soc. Dyers and Col., 1939, 55, 449—453).—Derivatives of the Naphtol AS series are hydrolysed by boiling KOH-EtOH, $(CH_2 \cdot NH_2)_2$, or mono-, di-, or tri-ethanolamine, to give the parent arylamine and acid (except where the acid component is $CH_2Ac \cdot CO_2H$, $CH_2Bz \cdot CO_2H$, or terephthaloyldiacetic acid, when it is destroyed). Naphtol AS-LC is the 4-chloro-2:5-dimethoxyanilide of 2:3-OH- $C_{10}H_6 \cdot CO_2H$ (I), and Naphtol AS-L4G, m.p. 200°, is 1-acetoacetamido-5-ethoxybenzthiazole. Constitutions are confirmed by synthesis from the appropriate acid, arylamine, and PCl_5 in PhMe or xylene, or in C_6H_5N at 115°. The following are also synthesised: the 2:4-dimethoxyanilide, m.p. 155°, 2-chloro-4-anisidide, m.p. 228°, 5-chloro-, m.p. 211°, and 5-bromo-2-anisidide, m.p. 216—217°, and 2-methoxy-5-diethylaminosulphonylanilide, m.p. 209—210° (3-amino-4-methoxybenzenesulphonodiethylamide has m.p. 105°), of (I), the anilide, m.p. 183°, o-toluidide, m.p. 164°, α -, m.p. 190—191°, and β -naphthylamide, new m.p. 202°, 2:5-dimethoxyanilide, m.p. 147—148°, 2-chloro-4-anisidide, m.p. 182°, 4-chloro-2:5-dimethoxyanilide, m.p. 192°, and 2-methoxy-5-diethylaminosulphonylanilide, m.p. 183—184°, of 5:6:7:8-tetrahydro-2-hydroxy-3-naphthoic acid (the Ac derivative of the parent acid has new m.p. 147°); the 4-methoxy-2-methylanilide, m.p. 243—244°, 2:5-dimethoxyanilide, m.p. 285°, 4-chloro-2:5-, m.p. 237°, and 5-chloro-2:4-dimethoxyanilide, m.p. 272°, and 2-methoxy-5-diethylaminosulphonylanilide, m.p. 245°, of 2-hydroxyanthracene-3-carboxylic acid; 1-benzoylacetamido-5-ethoxybenzthiazole, new m.p. 208°; and the bis-4-chloro-2:5-dimethoxyanilide, m.p. 255—256°, of terephthaloyldiacetic acid. A. T. P.

Action of benzamide and acetamide on dibenzoyl disulphide. L. SZPERL and L. RAKOWSKI (Rocz. Chem., 1939, 19, 409—412).—The following reactions occur in xylene at the b.p.: $Bz_2S_2 + NH_2Bz \rightarrow NHBz \cdot SBz + BzSH$; $NHBz \cdot SBz \rightarrow NHBz_2 + S$; $BzSH + NH_2Bz \rightarrow NHBz_2 + H_2S$; $Bz_2S_2 + NH_2Ac \rightarrow NHAc \cdot SBz + BzSH$; $NHAc \cdot SBz \rightarrow NHBzAc + S$; $BzSH + NH_2Ac \rightarrow NHBzAc + H_2S$; $NHBzAc + BzSH \rightarrow NHBz_2 + AcSH$. R. T.

Oxidisability of thioarylhydrazides to disulphides. H. WUYTS and A. LACOURT (Bull. Soc. chim. Belg., 1939, 48, 193—200).— $NHPh \cdot NH \cdot C(SPh)$ (I) is oxidised by air or by 1 + $NaHCO_3$ to the corresponding disulphide (II), $(NHPh \cdot N \cdot C(SPh)_2)_2$,

m.p. 149°, which is insol. in alkali, contains two active H, and yields a Ac_2 derivative. Similar disulphides, m.p. 165° (III) and —, are formed from $\text{NHPH}\cdot\text{NH}\cdot\text{CS}\cdot\text{C}_{10}\text{H}_7\cdot\alpha$ and $\text{NPhMe}\cdot\text{NH}\cdot\text{CS}\cdot\text{C}_6\text{H}_{11}$ whereas $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{SMe})\cdot\text{C}_6\text{H}_4\text{Me}\cdot p$ resists oxidation. Reduction of the disulphides by SnCl_2 and HCl regenerates the thiohydrazides. With MgMeI the reaction $(\text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{S})_2 + \text{MgMeI} = \text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{SMe} + \text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{SMgI}$ is quant. The product, m.p. 187°, derived from (I) is also obtained from (II) by the action of EtOH , CH_2O , and HCl . Similarly (III) yields a substance, m.p. 198°.

H. W.

Polyhydric alcohol-polybasic acid reactions. III. Glycerol-phthalic anhydride reaction. IV. Glyceryl phthalate from phthalic acid. R. H. KIENLE, P. A. VAN DER MEULEN, and F. E. PETKE (J. Amer. Chem. Soc., 1939, 61, 2258—2268, 2268—2271; cf. A., 1930, 1434).—III. Interaction of glycerol (2 mols.) and $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ (3 mols.) at $\sim 200^\circ$ is at first rapid and exothermic, owing to formation of glyceryl H phthalates, but then becomes slower. Periodic determination of H_2O evolved and of the acid and sap. val., mol. wt., analysis, and physical properties of the product show that the later reaction is mainly formation of large mols. by interesterification with smaller amounts of intra-esterification and anhydride-formation. Gelation occurs at fairly low mol. wts. and is dependent on the three-dimensional nature of the intertwining mols. Apparatus is described.

IV. Reaction of glycerol with $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ is essentially similar to the later stages of that with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, but differences in the early stages are noted.

R. S. C.

Derivatives of phthalylcarbamide. C. S. SMITH and C. J. CAVALLITO (J. Amer. Chem. Soc., 1939, 61, 2218—2221).—Figures in brackets below indicate relative hypnotic activity (all low) when injected (0.5 g. per kg. body-wt.; suspended in aq. glucose-glycerol) intraperitoneally into rats. Heating the appropriate acid anhydrides and carbamide derivatives, first at 124° and then with POCl_3 at 100° , gives "phthalylcarbamide," $o\text{-C}_6\text{H}_4(\text{CO}\cdot\text{NH})_2\text{CO}$ (35%) [0], m.p. 207—207.5°, and its *N-Me* (40%) [0], m.p. 190—192°, *N-allyl* (30%) [0], m.p. 135—?, *N-Ph* (48%) [1], m.p. partly 164—165°, remainder 194°, *N-o* (18%) [1], m.p. 190° (decomp., rapid), 200.5° (slow heating), *N-m* (38%) [1], m.p. 139°, and *N-p-tolyl* (21%) [3], m.p. 155—160°, *N-o* (17%) [1], m.p. 220°, and *N-p-phenetyl* (42%) [2], m.p. 196—198°, *N-o* (20%) [1], m.p. 218°, and *N-p-anisyl* derivatives (12%) [2], m.p. 199°, *phthalylthiocarbamide* (49%) [0], m.p. 181—181.5°, Δ^2 -*tetrahydro*- (19%) [0], m.p. 270°, 3- (57%) [4], m.p. 190° (decomp.), and 4-*nitro-phthalylcarbamide* (61%) [0], m.p. 206—207°, 3-*nitro-N*- or *N'-p-tolyl*- (38%) [3], m.p. 189—190°, and *p-phenetyl-carbamide* (35%) [0], m.p. 191—195°.

R. S. C.

Preparation of *N*-substituted phthalimides. G. WANAG (Latvij. Univ. Raksti, 1939, 4, 405—421).—*N*-Substituted phthalimides are rapidly and quantitatively obtained from $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ (I) and primary aromatic amines in boiling, glacial AcOH ;

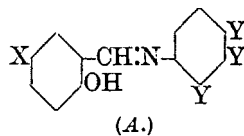
the disappearance of the amine is established by the colour test with bindone. The reactant ratio 1:1 is satisfactory since eventual $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, formed from the liberated H_2O and (I), reacts almost as rapidly as (I). Amine salts react slowly and incompletely but, with the exception of the nitrates, they can be employed if NaOAc is also added. Substituted anilines do not differ greatly from NH_2Ph in rapidity and completeness of reaction. The change can be extended to fatty and fatty-aromatic primary amines; the corresponding salts are nearly inactive unless NaOAc is present. Since *sec.* and *tert.* amines are not reactive they can be separated from primary amines by this method. (I) can be replaced by 3-nitrophthalic, succinic, or naphthalic anhydride. Dilution of AcOH is unwise. The following *-phthalimides* are described: phenyl-, m.p. 208°; *o*-, m.p. 183°, *m*-, m.p. 176°, and *p*-, m.p. 204°, *-tolyl*:- *o*-, m.p. 137°, and *p*-, m.p. 177°, *-ethylphenyl*:- 2:4-, m.p. 155°, 2:5-, m.p. 163°, 2:6-, m.p. 204°, and 3:5-, m.p. 135°, *-dimethylphenyl*:- 2:4:6-, m.p. 171°, and 2:4:5-, m.p. 147°, *trimethylphenyl*:- *o*-, m.p. 165°, *m*-, m.p. 154°, and *p*-, m.p. 285°, *-diphenyl*:- *p-triphenylmethylphenyl*-, m.p. 247°, 1-, m.p. 181°, and 2-, m.p. 216°, *-naphthyl*:- 1-*tetrahydro-naphthyl*-, m.p. 142°; 2-*fluorenyl*-, m.p. 288°; *p-acetamidophenyl*-, m.p. 283°; *p-anilinophenyl*-, m.p. 270°; *p-dimethylaminophenyl*-, m.p. 260°; methyl-, m.p. 134°; ethyl-, m.p. 78°; *isopropyl*-, m.p. 86°; *n-butyl*-, m.p. 34°; *isobutyl*-, m.p. 93°; *n-heptyl*-, m.p. 40°; *n-heptadecyl*-, m.p. 63°; *allyl*-, m.p. 70°; *benzyl*-, m.p. 115°; α -, m.p. 43—44°, and β -, m.p. 130°, *-phenylethyl*:- *benzhydryl*-, m.p. 225° (this compound is possibly 1:4-*diketo*-3:3-*diphenyl*-1:2:3:4-*tetrahydroisoquinoline*); 2-*tetrahydronaphthyl*-, m.p. 128°; *cyclohexyl*-, m.p. 168°; *camphyl*-, m.p. 55°.

H. W.

Δ^2 -4-Cholestadiene-3-acetic acid, m.p. 226°.—See B., 1939, 1077.

Phototropy of anils and of solutions of the leuco-cyanides of malachite- and brilliant-greens. V. DE GAOUCK and R. J. W. LE FÈVRE (J.C.S., 1939, 1457—1465).—Phototropy among anils appears to occur only in the solid state; in solution, no such changes of colour or other properties can be produced by illumination. Salicylidene-*m*-toluidine (I), one of the most phototropic anils, is examined in C_6H_6 , CCl_4 , or CHCl_3 , spectrophotometrically, and dielectrically (diagrams of apparatus). Absorption spectra of 11 other anils are examined. X-Ray examination of the two forms of (I) shows that, except for the colour, no other crystallographical property is changed by light. Phototropic mechanism must thus depend on intermol. resonance in the crystal lattice (diagrams given and mechanism discussed). Such mechanism should be influenced by factors tending to modify the H bond resonance, e.g., phototropic *o*- or *p*-hydroxyanils should lose this

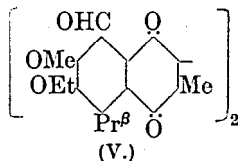
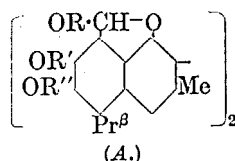
property if the H of the OH is methylated; methylation does destroy phototropy. Substituents in the aryl nuclei should have a great effect. Results with a no. of anils (type A; X = Me, Cl, Br, NO_2 , Y = H;



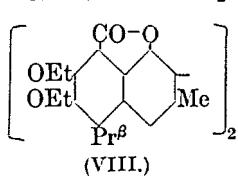
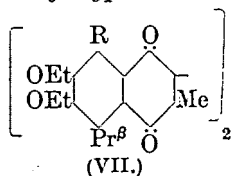
X = Me, 4-Y = NO₂; X = NO₂, 4-Y = Me; X = H, 4-Y = H, Me, Cl, Br, NO₂; X = H, 2- or 3-Y = Me) show that phototropy does not occur if X is other than H; influence of Y is marked, as although (I) and salicylidene-aniline (II) and -p-bromoaniline show phototropy, the corresponding -o- and -p-toluidine and -p-chloroaniline undergo no apparent colour change. (II) shows little colour development in sunlight, but if the light is first passed through a blue filter, a strong colour change is induced in the anil. The leuco-cyanides of malachite- and brilliant-green show phototropy in EtOH (owing to induced ionisation), but not in C₆H₆; their dipole moments, and that of leuco-malachite-green, illustrate facilitation of mesomerism by the NR₂ group. A. T. P.

Structure and absorption spectrum of o-phthalaldehyde acid.—See A., 1939, I, 507.

Structure of gossypol. XXII. Gossypol ethers and their reduction products. R. ADAMS and W. R. DIAL (J. Amer. Chem. Soc., 1939, 61, 2077—2082; cf. A., 1939, II, 320).—Gossypol ethers and some reactions thereof are described. Addition of 20% KOH-EtOH to gossypol Me₄ ether (I) and Et₂SO₄ in warm C₆H₆ gives the Me₄ Et₂ ether (II) (A; R = R' = Me; R'' = Et), m.p. 271—272° or 228—229° [with AcOH-NHPh·NH₂ gives the phenylhydrazone (III), m.p. 268—269°, of gossypol Me₂ Et₂



ether], also obtained from gossypol Et₂ ether (IV) (phenylhydrazone, m.p. 260—261°) by Me₂SO₄-KOH-MeOH. With a little H₂SO₄ in AcOH at 100°, (II) gives (IV). HCl-MeOH reconverts (III) into (II), and HCl-EtOH gives a Me₂ Et₄ ether (A; R' = Me; R = R'' = Et), m.p. 241—242°. Dil. HNO₃ oxidises (II) to norgossic acid Me Et ether [6-carboxy-5-methoxy-4-ethoxy-3-isopropylphthalic anhydride], m.p. 178—179°. CrO₃-AcOH oxidises (II) to gossypolone Me₂ Et₂ ether (V), m.p. 185—186°. Gossypol Et₆ ether (VI) gives the Et₄ ether phenylhydrazone, m.p. 241—242°, converted by HCl-MeOH into the Me₂ Et₄ ether (A; R = Me; R' = R'' = Et), m.p. 206—207°. With conc. HNO₃-H₂O (1:4 by vol.), (VI) gives gossypolonic acid Et₄ ether [(VII); R = CO₂H],



m.p. 272—273°, and with CrO₃-AcOH gives gossypolone Et₄ ether [(VII); R = CHO], m.p. 146—147°, and gossylic acid lactone Et₄ ether (VIII), m.p. 244—245° [(NO₂)₂-derivative, m.p. 266—267°]. H₂-PtO₂ in AcOH (not EtOH or EtOAc) at 50°/3 atm. reduces gossypol Me₆ ether (IX) to deoxygossypol Me₄ ether

(X) (B; R = R' = Me), m.p. 261—263° (decomp.). PhN₂HSO₄ couples with gossylic acid Me₄ ether, but not with (IX) or (X); 2:4:1-

(NO₂)₂C₆H₃·N₂HSO₄ couples with all three compounds. With HNO₃, (X) gives gossic acid, and with CrO₃ in boiling AcOH gives gossypolone Me₄ ether. Hydrogenation of (A; R = Et; R' = R'' = Me) gives (B; R = R' = Me), but that of (A; R = R' = Me; R'' = Et) gives deoxygossypol Me₂ Et₂ ether (B; R = Me; R' = Et), m.p. 240—242°; that of (I) [= (A; R = R' = Me; R'' = H)] gives an indefinite product, whence (B; R = R' = Me) or (R = Me; R' = Et) were obtained. M.p. are corr. R. S. C.

Reactions of bromomagnesium enolates of mesityl ketones. II. Condensation. R. C. FUSON, W. O. FUGATE, and C. H. FISHER (J. Amer. Chem. Soc., 1939, 61, 2362—2365; cf. A., 1939, II, 373).—The MgBr derivative (I) of acetomesitylene reacts as 2:4:6-C₆H₂Me₃·CO·CH₂·MgBr. With 0.5 mol. of RCOCl it yields 2:4:6-C₆H₂Me₃·CO·CH₂·COR [R = Me (II) or Ph], but with more RCOCl yields 2:4:6-C₆H₂Me₃·CO·CH(COR)₂. With 2:4:6-C₆H₂R₃·COCl (R = Me or Et), it gives only 2:4:6:2':4':6'-hexamethyl- (Cu derivative) and 2:4:6-trimethyl-2':4':6'-triethyl-dibenzoylmethane, b.p. 188—190°/2 mm. (Cu derivative, m.p. 287°). With EtOAc, (I) gives 26% of (II), and with HCO₂Et gives 33% of ω-hydroxymethyleneacetomesitylene, b.p. 108—110°/3 mm. (Cu derivative). The appropriate MgBr derivative with CO₂ in Et₂O gives β-keto-β-mesitylpropionic, m.p. 104—105°, α-2:4:6-trimethylbenzoyl-propionic, m.p. 111.5—112.5°, and isobutyric, m.p. 86—87°, and α-3:5-dibromo-2:4:6-trimethylbenzoylisobutyric acid, m.p. 108—110°. With PhCHO, (I) gives γ-keto-α-phenyl-γ-mesityl-n-propyl alcohol (47%), m.p. 77—77.5°, and 26% of 2:4:6-C₆H₂Me₃·CO·CH:CHPh. 2:1-OMe·C₁₀H₆·CHO and (I) in C₆H₆-Et₂O give 82% of mesityl β-2-methoxy-1-naphthylvinyl ketone, m.p. 107—108° (dibromide, m.p. 148—149°). With COPhMe, (I) gives 2:4:6-C₆H₂Me₃·CO·CH:CPhMe, m.p. 85.5—87° (lit. 84°), and with COPh₂ gives 2:4:6-C₆H₂Me₃·CO·CH₂·CPh₂·OH, m.p. 74—75°. Br converts (I) only into 2:4:6-C₆H₂Me₃·CO·CH₂Br, but anhyd. CuCl in hot Et₂O gives a little (2:4:6-C₆H₂Me₃·CO·CH₂)₂. 2:4:6-C₆H₂Me₃·CO·CH:CH₂ and (I) give 82% of (2:4:6-C₆H₂Me₃·CO·CH₂)₂CH₂. R. S. C.

Lignin and related compounds. XLV. Synthesis and properties of α-hydroxypropiovanillone. A. B. CRAMER and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 2204—2206).—o-C₆H₄(OMe)₂, CHMeBr·COBr, and AlCl₃ in CS₂ at room temp. give α-bromopropiovanillone (35%), m.p. 105—106°, unstable (prolonged heating) in solvents in which it is only slightly sol., which with Ac₂O-NaOAc at 100° gives α-acetoxypropiovanillone acetate (84%), m.p. 122—123°, hydrolysed by hot KOH-MeOH to α-hydroxypropiovanillone (I) (92%), m.p. 109—110°. With 0.5% dry HCl-EtOH this gives α-ethoxypropiovanillone, b.p. 125—140°/0.005 mm., with CH₂N₂-

Et_2O gives α -hydroxypropioveratrone, b.p. 130—150°/0.01 mm., with MgMeI shows 1.75 active H and 0.75 CO (low vals. due to OH p - to CO), and with boiling 5% aq. H_2SO_4 , 5% dry HCl - MeOH , or 95% HCO_2H gives brown, amorphous products ($\sim 70\%$ C). (I) is a possible precursor of lignin.

R. S. C.

Action of magnesium isobutyl bromide on 3:4:5-trimethoxybenzonitrile. H. L. HALLER and P. S. SCHAEFFER (J. Amer. Chem. Soc., 1939, 61, 2175—2177).—3:5:1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NH}_2$ with PCl_5 gives a product, $\text{C}_9\text{H}_8\text{O}_2\text{NCl}$, m.p. 124—125°, but with P_2O_5 gives 3:5-dimethoxybenzonitrile, m.p. 87—88°, which with $\text{MgBu}^\beta\text{Br}$ in Et_2O gives 45—50% of 3:5:1-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{COBu}^\beta$, b.p. 143—145°/2 mm. (semicarbazone, m.p. 195—196°). This ketone resists H_2 -Pd-C and gives unsatisfactory products with Na-EtOH or Zn-Hg-HCl. 3:4:5:1-(OMe) $_3\text{C}_6\text{H}_2\cdot\text{CN}$ (prepared from the amide by PCl_5) and $\text{MgBu}^\beta\text{Br}$ in Et_2O -PhMe give 3:4:5-trimethoxyphenyl Bu^β ketone, b.p. 147—150°/1 mm. (semicarbazone, m.p. 205°), ? 4-hydroxy-3:5-dimethoxyphenyl Bu^β ketone, m.p. 94° (faint green FeCl_3 reaction; semicarbazone, m.p. 162.5°; oxime, m.p. 110°; benzoate, m.p. 111°), and ? 3:5-dimethoxy-4-butylphenyl Bu^β ketone, b.p. 128—130°/0.35 mm. (semicarbazone, m.p. 184°).

R. S. C.

Methylation of β -ketonitriles. R. C. FUSON and D. E. WOLF (J. Amer. Chem. Soc., 1939, 61, 1940—1942).— p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ (prep. from p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ by conc., aq. KCN in EtOH) with Me_2SO_4 and aq. KOH at 70—130° (bath) gives only the *O*-Me ether, m.p. 58.5—59.5°, of the enol, but with boiling MeI -NaOEt-EtOH gives only *p*-bromo- α -cyanopropiophenone, m.p. 74.4—75.5°, obtained also from p - $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{Et}$, EtCN, and NaOEt, first at 80° and then at 110—120°. 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ with MeI -NaOEt-EtOH undergoes approx. equal amounts of *O*- and *C*-methylation (cf. A., 1938, II, 279). M.p. are corr. R. S. C.

Acylins from *tert*-butylglyoxal. R. C. FUSON, H. GRAY, and J. J. GOUZA (J. Amer. Chem. Soc., 1939, 61, 1937—1940).— $\text{Bu}^\gamma\text{CO}\cdot\text{CHO}$ (prep. from COMeBu^γ by SeO_2 in $\text{MeOH}\cdot\text{H}_2\text{O}$), b.p. 114—115°, +0.5 H_2O , m.p. 91—92° (softens at 85°; lit., m.p. 85°) (2:4-dinitrophenylhydrazones, m.p. 171—172°; phenylhydrazones, m.p. 119—120°; osazones, m.p. 119.5—120°; semicarbazones, m.p. 134—135°; di-oxime, m.p. 100.5—101.5°; gives 6- or 7-nitro-2-*tert*-butylquinoxaline, m.p. 134.5—135°), with 25% aq. NaOH at room temp. gives OH- $\text{CHBu}^\gamma\cdot\text{CO}_2\text{H}$, and with AlCl_3 and C_6H_6 gives phenylpivalylcarbinol [β -keto- α -phenyl- $\gamma\gamma$ -dimethyl-*n*-butan- α -ol], m.p. 46—47°, b.p. 90—102°/2 mm. (2:4-dinitrophenylhydrazones, m.p. 174—175°; benzoate, m.p. 96—97°). Similarly are obtained *p*-tolyl-, m.p. 48—49°, *m*-xylyl- (A), b.p. 133—135°/4 mm., and mesityl-pivalylcarbinol, m.p. 118—118.5°. Conc. HNO_3 at 100° converts the acylins into Ph (I), b.p. 75—76°/1 mm., *p*-tolyl (II), b.p. 97—97.5°/1 mm., *m*-xylyl (III), b.p. 103—104°/1 mm., and mesityl Bu^γ diketone (IV) (isolated by further heating as 3- NO_2 -derivative, m.p. 58—59°). (I) and (II) give quinoxaline derivatives, m.p. 108—109° and 109—110°, respectively, but (III) and (IV) do not react with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$. Some *di*-*m*-xylyl-

pivalylmethane [$\alpha\alpha$ -*di*-*m*-xylyl- $\gamma\gamma$ -dimethyl-*n*-butan- β -one], m.p. 111.5—112°, accompanies (A). $\text{HNO}_3\cdot\text{H}_2\text{SO}_4$ at 0° converts (III) into 3:5:2:4:1-(NO_2) $_5\text{C}_6\text{HMe}_2\cdot\text{CO}_2\text{H}$, new m.p. 202—203°. KOH-aq. EtOH converts (I) into $\beta\beta\beta$ -trimethylatrolactic [α -hydroxy- α -phenyl- $\beta\beta$ -dimethyl-*n*-butyric] acid, m.p. 105—106°. Na, followed by BzCl , converts (I) in PhMe- N_2 into $\alpha\beta$ -dibenzoyloxy- α -phenyl- $\gamma\gamma$ -dimethyl- Δ^{α} -*n*-butene, m.p. 138—139°.

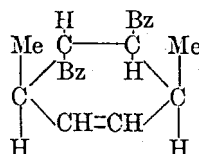
R. S. C.

Two isomeric 2-acetyldecahydronaphthalenes. G. CAUQUIL (Compt. rend., 1939, 209, 441—443).—Chlorination of a mixture of *cis*- and *trans*-decahydronaphthalene (obtained from $\text{C}_{10}\text{H}_8\cdot\text{Ni}\cdot\text{H}_2$) gives a mixture, b.p. 115°/18 mm., of *cis*- and *trans*- β -chlorodecahydronaphthalene, the Mg derivative of which with MeCHO gives 2-decahydronaphthylmethylcarbinol, b.p. 136—138°/14 mm., oxidised ($\text{CrO}_3\cdot\text{AcOH}$) to a mixture b.p. 128—132°/13 mm., of 2-acetyldecahydronaphthalenes, separated through the semicarbazones into the *trans*-, b.p. 142—143°/22 mm. (oxime, m.p. 104°; semicarbazone, m.p. 242°), and *cis*-isomerides, b.p. 138°/22 mm. (oxime, an oil; semicarbazone, m.p. 196°).

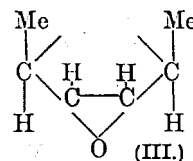
J. L. D.

Structure and absorption spectrum of phthalonic acid.—See A., 1939, I, 507.

Structure of gossypol. XXIII. Attempts to prepare desapogossypolone tetramethyl ether. Condensation of Δ^8 -hexadiene with dibenzoyl-ethylene. R. ADAMS and T. A. GEISSMAN (J. Amer. Chem. Soc., 1939, 61, 2083—2089).— $\text{CHMe}\cdot\text{CH}\cdot\text{CHEt}\cdot\text{OH}$ (prepared in 83% yield from $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$ and MgEtBr in Et_2O at 15—20°), b.p. 55°/15 mm., distilled with 48% HBr gives 67% of $(\text{CHMe}\cdot\text{CH})_2$, which (41 g.) with *trans*-(CHBz) $_2$ (60 g.) in PhMe (75 c.c.) gives 1:2-dibenzoyl-3:6-dimethyl- Δ^4 -cyclohexene (I) (53 g.), m.p. 136—137°, with a stereoisomeride (6.5 g.), m.p. 86—88° [dibromide, m.p. 152° (decomp.)]. Oxidation of (I) by many reagents gives indefinite results, the $\text{CH}\cdot\text{CO}$ reacting as well as the $\text{C}\cdot\text{C}$; its dibromide (II), m.p. 169—170°, with $\text{NaOAc}\cdot\text{AcOH}\cdot\text{Ac}_2\text{O}$ gives an isomeric dibromide, m.p. 202.5—203° (decomp.). With *o*- $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (1 mol.) in $\text{CHCl}_3\cdot\text{Et}_2\text{O}$ at 0°, (I) gives oxides, (III), m.p. 187.5—188°, and (IV), m.p. 154—155°. If the Bz are *trans*, (I) thus has the structure shown. With hot 25% $\text{H}_2\text{SO}_4\cdot\text{COMe}_2$ (1:4),



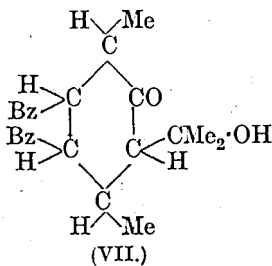
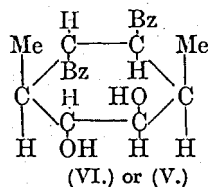
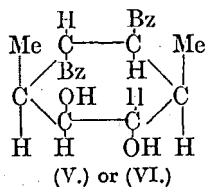
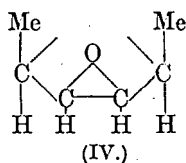
(I.)



(III.)

(III) gives mainly 4:5-dibenzoyl-3:6-dimethylcyclohexane-1:2-diol (V), m.p. 173—175°, with less of the isomeric diol (VI), m.p. 212—213°; (IV) gives similarly mainly (VI) with some (V), but an impure specimen yielded also a substance [? (VII)], $\text{C}_{25}\text{H}_{28}\text{O}_4$, m.p. 187—188° (no CO reactions; gives no CHI_3 in dioxan). With $\text{HIO}_4\cdot\text{AcOH}$ (no oxidation occurs) at room temp. or 25% $\text{H}_2\text{SO}_4\cdot\text{AcOH}$ (1:3) at 100°, (IV) gives 4:5-dibenzoyl-2-acetoxy-3:6-dimethylcyclo-

hexan-1-ol, m.p. 207°, hydrolysed by hot NaOMe-MeOH to (VI). With m-aq. HIO₄ in boiling COMe₂,



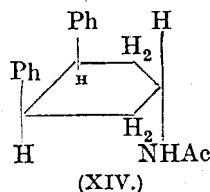
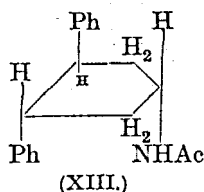
(IV) gives a product, C₂₄H₂₆O₅, m.p. 177—178° (decomp.). Pb(OAc)₄ in AcOH converts (VI) into a product, m.p. 170—170.5° (decomp.). A trace of 85% H₃PO₄ in boiling AcOH-Ac₂O dehydrates (I), yielding 1:2-diphenyl-3:6-dimethyl-3:6-dihydroisobenzofuran (VIII), m.p. 114—115°; the 4:5-dibromide (IX), m.p. 168—170° (decomp.), thereof is obtained therefrom or by a little H₂SO₄ in AcCl from (II), and with boiling C₆H₅N (not NaOAc-AcOH) gives 1:2-diphenyl-3:6-dimethylisobenzofuran (X), m.p. 129—131°. With maleic anhydride in Et₂O or C₆H₆, (X) gives 1:4-oxido-1:4-diphenyl-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic anhydride (70%), m.p. 310—312° (decomp.). (II) and C₆H₅N at 100° give 2:3-dibenzoyl-p-xylene, m.p. 144—145° [and (I)], obtained also from (VIII) by Br and NaOAc in boiling AcOH or, less well, from (I) by Br-C₆H₅N or (IX) by Br-NaOAc-AcOH, and reduced by Zn dust in NaOH-EtOH to 2:3-di-(α-hydroxybenzyl)-p-xylene, m.p. 149—151°. R. S. C.

Reactive methylene groups and nitroso-compounds. Abnormal action of acids on 1:2:3-triketones. A. SCHÖNBERG and R. C. AZZAM [with R. MICHAELIS] (J.C.S., 1939, 1428—1430; cf. A., 1937, II, 249).—CH₂PhBz and p-NO-C₆H₄·NMe₂-EtOH-piperidine at 100° (bath) give benzil-p-dimethylaminoanil oxide (I), m.p. 165—166°, and -dimethylaminoanil (II), m.p. 137—138° [the (II), m.p. 166°, of Skraup *et al.* (A., 1926, 722) is actually (I)]. (I) or (II) and H₂SO₄-H₂O (1:1) at 100° give Bz₂. CH₂Bz₂ and PhNO-EtOH give Ph₂ triketone β-anil oxide (III), m.p. 144—145° (decomp.), converted by hot H₂SO₄-H₂O (1:1) into Bz₂. Thus (III) is probably first hydrolysed to COBz₂, which undergoes rearrangement, subsequent loss of CO₂ to benzoin, and final oxidation (see below). CH₂Bz₂ and p-NO-C₆H₄·NMe₂-95% EtOH-Na₂CO₃ at 50—55° give Ph₂ triketone β-p-dimethylaminoanil oxide, m.p. 183—185° (decomp.). CH₂Bz·CO·C₆H₄Me-p and PhNO-EtOH give a mixture of isomeric (probably geometrical) Ph p-tolyl triketone β-anil oxides, m.p. 141—143° and 132—134°. COBz₂ with boiling H₃PO₄ (d 1.7) gives benzoin, but H₂SO₄-H₂O (1:1), or AlCl₃ at 100°, affords Bz₂. Benzoin and H₂SO₄-H₂O (1:1) also give Bz₂. Tri-

keto-hydrindene hydrate and boiling H₂SO₄-H₂O (1:1) give bisindanedione, m.p. ~297°. A. T. P.

1-Hydrindone. C. C. PRICE and F. M. LEWIS (J. Amer. Chem. Soc., 1939, 61, 2553—2554).—Ph-[CH₂]₂-CO₂H and, best, 5% oleum at 140° (5 min.) give 27% of 1-hydrindone. Addition of BF₃ or AlCl₃ lowers the yield. R. S. C.

Anionotropic and prototropic changes in cyclic systems. VII. Structure of the chlorodiphenylcyclopentenone obtained by action of hydrogen chloride on anhydroacetonebenzil. H. BURTON and C. W. SHOPPEE (J.C.S., 1939, 1408—1415).—Further evidence (cf. A., 1934, 409) is presented for formulating the compound (I), m.p. 129°, from anhydroacetonebenzil and EtOH-HCl as 2-chloro-3:4-diphenyl-Δ²-cyclopentenone (II). The argument of Allen *et al.* (A., 1937, II, 457) that structure (II) must be assigned to the compound (III), m.p. 142°, obtained from POCl₃ and 2-hydroxy-3:4-diphenyl-Δ²-cyclopentenone (IV), an enolic form of 3:4-diphenylcyclopentane-1:2-dione (V) is invalid, since (V) can also enolise to 2-hydroxy-4:5-diphenyl-Δ²-cyclopentenone (VI). Further, either (III) [improved prep.; also obtained from 2:3-diphenylcyclopentenone (VII) and SO₂Cl₂ in C₆H₆ at 15°] or (IV, VI) is reduced by P-HI-AcOH to (VII), which is hydrogenated (cf. A., 1939, II, 269) to trans-2:3-diphenylcyclopentanone (VIII), also obtainable by direct hydrogenation (PtO₂ with NaOAc, 3H₂O in EtOH; Pt-black with NaOAc and NH₂OH, HCl in EtOH) of (III). Therefore CO in (III) is unsymmetrical to the Ph groups, and (III) is regarded as a 2-chloro-4:5-diphenylcyclopentenone (IX), derived from (VI), not (IV). In contrast, (I) with P-HI-AcOH gives 3:4-diphenyl-Δ³-cyclopentenone (X), and this [or (I)] is catalytically reduced to cis-3:4-diphenylcyclopentanone. (I) gives an almost quantitative yield of its oxime (XI), m.p. 172°; with NH₂OH at <40° the only product from (III) is a dimeric oxime, C₃₄H₂₆O₂N₂, m.p. 258—259° (decomp.). With piperonal-HCl, (I) forms a piperonylidene derivative, m.p. 165°, but (III) gives a compound (dimeric?), m.p. 188—189° (decomp. 210—215°). The formation of desylactic acid (XII) from (III) and O₃ in AcOH (Allen *et al.*, *loc. cit.*) is not confirmed; the only identifiable product from this reaction (or from oxidation by KMnO₄ in 90% COMe₂ at -15° in presence of MgSO₄, or by CrO₃ in 90% AcOH at 43°) is BzOH. Oxidation of (I) by KMnO₄ in COMe₂ at 15° to (XII) (cf. A., 1934, 409) is confirmed. Possible tautomerism of (IX), which is best regarded as a mixture of interchangeable isomerides, is considered. Reduction (best catalytic) of (XI) in AcOH gives



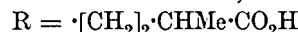
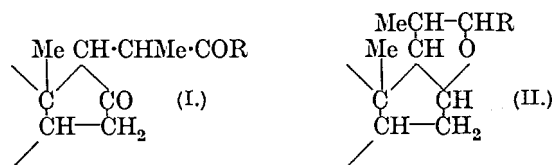
trans-3:4-diphenylcyclopentylamine, m.p. 119—120° [picrate, m.p. 232° (decomp.); Ac derivative (XIII), m.p. 119°]. trans- and cis-3:4-Diphenylcyclo-

pentanoneoxime are reduced (Na in EtOH) respectively to (XIII) and a mixture of two *cis*-3:4-diphenylcyclopentylamines [Ac derivatives (XIV) or (XV), m.p. 133—134°, and (XV) or (XIV), m.p. 128°]. The oxime, m.p. 179°, of (X) is reduced and then acetylated to (XIII). The oxime of (VIII) is reduced and acetylated to two 1-acetamido-2:3-diphenylcyclopentanes, m.p. 187° and 170—171° (both slight previous sintering), also obtained by reducing the oxime of (VII). $\gamma\delta$ -Diphenyl- Δ^4 -pentenoic acid (cf. A., 1937, II, 247; a liquid isomeride is simultaneously formed) (*anilide*, m.p. 129—130°) is hydrogenated to $\gamma\delta$ -diphenyl-*n*-valeric acid (*anilide*, m.p. 111—112°). An attempt to use its *Me* ester, b.p. 206—208°/15 mm., to synthesise (VIII) by the Dieckmann reaction was unsuccessful; a semi-solid product, yielding a semicarbazone (?), m.p. 237° (decomp.), was formed. E. W. W.

Wolff-Kishner reduction of steroid ketones. J. D. DUTCHER and O. WINTERSTEINER (J. Amer. Chem. Soc., 1939, 61, 1992—2000).—With 7 steroid ketones it is shown that NaOEt at 180° reduces a C:N:NH:CO:NH₂ at position 3 mainly to CH:OH (mixed epimerides; mostly that with the OH *trans* to the H on C₅), but that a similar group at position 7 or 12 gives only CH₂, and that presence of the latter reduces the amount of OH formed at C₃. Cholestenonesemicarbazone gives Δ^4 -cholestene, $\alpha\beta$ -unsaturated and saturated alcohols. Hydrazones and ketazines react similarly. With any derivative an added excess of N₂H₄·H₂O greatly suppresses formation of CH:OH. Time of heating (4·5—22 hr.), presence of H₂O, or exclusion of O₂ has little effect. Increase of temp. from 180° to 200° slightly favours formation of CH₂ from cholestanonesemicarbazone. It is considered that the semicarbazones give the hydrazones, which are either reduced to hydrocarbons or hydrolysed to ketones, which with NaOEt give the alcohols and MeCHO. The alcohols are separated from hydrocarbons as H succinates or, less well, H phthalates. The following are described. Cholestanone-, sinters at 227°, decomp. 238°, coprostanone-, sinters at 178°, decomp. 192°, cholestenone-, m.p. 215—235° (decomp.), and *dehydrolithocholic acid semicarbazone*, m.p. 230° (decomp.); β -cholestanyl H phthalate, m.p. 160°, and succinate, m.p. 171°; α -coprostanyl H phthalate, m.p. 218—220°; cholestanone-hydrazine, softens at 230°, m.p. 248° (decomp.), and -ketazine, decomp. ~200°; cholestenoneketazine, decomp. > 190°; *dehydrodeoxycholic acid disemicarbazone*, discolours at 190°, decomp. 215°; Et α -3-hydroxy-12-ketocholanoate H succinate, m.p. 170°, [α]_D +96·3—95·7° in EtOH; Et α -lithocholate H succinate, m.p. 147°. R. S. C.

Sterols. LXIX. Oxidation products of sarsapogenin. Sarsapogenenic acid and related substances. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 2072—2077).—Sarsapogenenic acid (I) probably contains the grouping shown. It is reduced by H₂-PtO₂ in AcOH at 25°/3 atm. to anhydrotetrahydrosarsapogenenic acid (II) (Fieser *et al.*, A., 1939, II, 31), m.p. 183—187° [*Me*

ester, m.p. 125—127° (benzoate, m.p. 140—141·5°)], which appears to be identical with sarsapogenenic



acid (A., 1939, II, 276), and with CrO₃-AcOH at room temp. gives the 3-dehydroanhydro-acid, m.p. 196—199°. Na + EtOH convert (I) into tetrahydrosarsapogenenic acid, m.p. 179—181° (decomp.) or 194—196°, obtained also by catalytic hydrogenation of anhydrosarsapogenenic acid (III); (I) is converted by Al(OPrⁱ)₃ into a substance, C₂₇H₄₄O₅, m.p. 206—208° (decomp.) (poor yield). With CrO₃-80% AcOH, (I) gives 3-dehydrosarsapogenenic acid, m.p. 163—164° (cf. Jacobs and Simpson's acid, m.p. 162°; A., 1935, 864) (*Me* ester, m.p. 125°), which gives a 4-*Br*-derivative, m.p. 188·5—191°, and thence by hot C₅H₅N 3-dehydro- $\Delta^{4,5}$ -sarsapogenenic acid, m.p. 199—201°. When (I) (as 3-acetate) is oxidised by CrO₃ in 80% AcOH at 80—85°, no neutral fraction is obtained, but 5% of the acid, C₂₂H₃₄O₄, m.p. 287° (decomp.) (A., 1939, II, 322), is isolated. KOH in aq. EtOH converts (I) into (III), m.p. 242—244° (decomp.) [no semicarbazone; unaffected by Al(OPrⁱ)₃-PrⁱOH], but Fieser and Jacobsen's method (A., 1938, II, 108) gives also an isomeric acid, m.p. 181—184° (decomp.), converted into (III) by hot NaOH-aq. EtOH. Analysis of (III) and derivatives shows that it is C₂₇H₄₀O₄ (not H₄₂). Its structure is discussed. The dibasic acid (*loc. cit.*) [*Me*₂ ester, m.p. 161—162° (*acetate*, m.p. 158—160°)] of Fieser *et al.* is C₂₇H₄₀O₇. The neutral acetate, m.p. 162—164°, obtained from sarsapogenin acetate by CrO₃, is hydrolysed to a 3-OH-compound, C₂₇H₄₂₋₄₄O₅, m.p. 215—217°, gives a semicarbazone, m.p. 249—251° (decomp.), with H₂-PtO₂ in AcOH-EtOH (10:3) (not in EtOH) at 25°/3 atm., followed by KOH-EtOH, gives a substance, C₂₇H₄₆₋₄₈O₄, m.p. 215—217°, and with Zn-Hg-HCl-EtOH gives tetrahydrosarsapogenin. R. S. C.

Estrogens with oxygen in ring B. I. 7-Keto- and 7-hydroxy- α -estrone. W. H. PEARLMAN and O. WINTERSTEINER (J. Biol. Chem., 1939, 130, 35—45).—7:8-Dihydroxy α -estrone (prep. from equilin acetate by OsO₄, followed by Na₂SO₃), forms, m.p. 253—254° and 210—216° (variable), [α]_D²⁵ +135—139° in dioxan (cf. A., 1938, II, 102), when distilled at 205—210°/0·003 mm., gives 7-keto α -estrone (I), m.p. 212—212·5° (decomp.), [α]_D²⁵ +167° in dioxan [spectrum identical with that of α -estrone (II); *dioxime*, decomp. 252—253°; *enol diacetate* (III), m.p. 171—171·5°, showing absorption max. at 2680 (ϵ 9680) and min. at 2415 A. (ϵ 4320) indicating conjugation of C:C with the aromatic ring], unstable to alkali. The *disemicarbazone*, m.p. >295°, of (I) and NaOEt-EtOH at 185° give the same 7-deoxy α -estrone, new m.p. 135·5—137·5°, [α]_D²⁵ +72° in EtOH (benzoate, new m.p. 172·5°), as is obtained from α -estrone, which proves the stereochemical configuration of (I). H₂-

Pd in AcOH rapidly converts (III) into 7-hydroxy- α -estrone diacetate, dimorphic, m.p. 122–123° and 131–131.5° [absorption max. at 2690 (ϵ 660) and min. at 2510 A. (ϵ 350)], hydrolysed by hot alkali to 7-hydroxy- α -estrone (IV), m.p. 265–267° (decomp.), $[\alpha]_D^{25} +134.5^\circ$ in dioxan (3-benzoate, m.p. 181°). (I) and (IV) are 0.003 as active physiologically as is (II). m.p. are corr. R. S. C.

Synthesis of substances related to the sterols. XXVII. Synthesis of α -nor α -estrone. (SIR) R. ROBINSON and H. N. RYDON (J.C.S., 1939, 1394–1405).—The structure of 2 : 6- $C_{10}H_6AcOMe$ (modified prep.; cf. Haworth and Sheldrick, A., 1934, 885), important as starting material for 3'-keto-4-acetoxy-7-methoxy-1 : 2-cyclopentenophenanthrene (I) (modified prep.; cf. Robinson, A., 1938, II, 496), is confirmed by converting its oxime, m.p. 169–170°, by PCl_5-Et_2O into 6-acetamido-2-methoxynaphthalene, m.p. 162–163°, and this (HCl; HNO_2 ; Me_2SO_4) into 2 : 6- $C_{10}H_6(OMe)_2$. Conversion of compounds of the type of (I) into hydro-derivatives related to α -estrone cannot be effected by direct hydrogenation. Thus, H_2-PtO_2 in AcOH at 70° and (I) give small amounts of 4 : 3'-dihydroxy-7-methoxy-, m.p. 139–140°, and 3'-hydroxy-4-acetoxy-7-methoxy-1 : 2-cyclopentenophenanthrene, m.p. 145°, with non-cryst. products. Hydrolysis (KOH-MeOH) of the crude hydrogenation product from (I) yields 4-hydroxy-7-methoxy-1 : 2 : 3 : 4-tetrahydro-1 : 2-cyclopentenophenanthrene, m.p. 141–142° (p-nitrobenzoate, m.p. 214–216°; digitonide) (stable to CrO_3 -AcOH), and two oily fractions. Dehydrogenation (Pd-C) of that of lower b.p. gives 1 : 2-cyclopentenophenanthrene (II); of the higher, (II) and 7-methoxy-1 : 2-cyclopentenophenanthrene. Formation of the last indicates preferential deoxygenation in the 4-position in the hydrogenation of 4 : 7-dihydroxyphenanthrene derivatives. To obtain 3'-keto-compounds, it was decided to open the 5-membered ring before hydrogenation. 3'-Keto-4 : 7-dimethoxy-1 : 2-cyclopentenophenanthrene (III) [prep. from (I) and NaOH-EtOH; Me_2SO_4] [2'-oximino-derivative, m.p. 248–249° (decomp.), from (III), $KOBu^+$, and $iso-C_5H_{11} \cdot O \cdot NO$] with $HCO_2Et-NaOEt-EtOH$ in C_5H_5N , followed by AcOH, gives its 2'-formyl derivative, decomp. 195°, which with AcOH- NH_2OH , HCl at 70° yields the 2'-CN-derivative. The last is hydrolysed (aq. KOH-EtOH) to 4 : 7-di-

m.p. 138–140°, and (main product) 7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-1- β -propionic-2-carboxylic acid (VII), m.p. 142–143°. The Pb salt of (VII) heated at 0.25 mm. gives the Me ether (VIII), m.p. 142–143°, demethylated (AcOH-HI at 140°) to α -nor α -estrone [7-hydroxy-3'-keto-

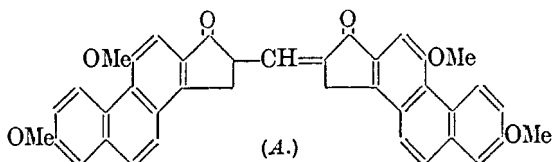
1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-1 : 2-cyclopentenophenanthrene] (IX), m.p. 222° (acetate, m.p. 145–146°), in which α denotes indeterminate (probably *cis-cis*) configuration. The Pb salt of (V) similarly gives 3'-keto-4 : 7-dimethoxy-9 : 10-dihydro-1 : 2-cyclopentenophenanthrene, m.p. 143° [depressed by admixed (VIII)] (2 : 4-dinitrophenylhydrazones, m.p. 242–243°); the reaction fails with (VI).

4-Hydroxy-3'-keto-7-methoxy-1 : 2-cyclopentenophenanthrene [oxime (+ H_2O), m.p. 268°] in EtOH with Et_2SO_4 in aq. NaOH gives the 7-methoxy-4-ethoxy-compound, m.p. 194°, which, as before, gives via the 2'-formyl the 2'-CN-derivative, hydrolysed to 7-methoxy-4-ethoxyphenanthrene-1- β -propionic-2-carboxylic acid, m.p. 268–269°, the Me_2 ester, m.p. 118° (purified as before), of which is hydrogenated to 7-methoxy-4-ethoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene-1- β -propionic-2-carboxylic acid, m.p. 160° (no other product isolated).

$\gamma\gamma$ -Diketo- γ -(6-methoxy-2-naphthyl)heptonic acid (A., 1938, II, 496) is demethylated (AcOH-HCl) to the 6-OH-acid, m.p. 171–172°, which with hot aq. KOH gives 3-(6'-hydroxy- β -naphthyl)- Δ^2 -cyclopentenone-2-acetic acid, m.p. 221–222°, cyclised (Ac_2O) to the Ac_2 derivative, m.p. 196–197° (decomp.), of 4 : 7-dihydroxy-3'-keto-1 : 2-cyclopentenophenanthrene, m.p. 338° (decomp.), methylated to (III).

With the product from Et cyclopentanone-2-carboxylate and K in C_6H_6 , $m-OMe-C_6H_4-[CH_2]_2-CH_2I$ (improved prep.) gives Et 2-(γ -m-anisylpropyl)cyclopentanone-2-carboxylate, b.p. 187–190°/0.5 mm. [semicarbazone (+2MeOH)], which on hydrolysis and heating with Ac_2O at 260–270°/100 mm. gives 2-(γ -m-anisylpropyl)cyclopentanone, b.p. 173–177°/0.8 mm. [semicarbazone, (+EtOH) m.p. 180°; 2 : 4-dinitrophenylhydrazones, m.p. 103–104°]. E. W. W.

Action of alcoholic monomethylamine on derivatives of benzoquinone and toluquinone. I. Methoxy- and hydroxy-methoxy-derivatives. W. K. ANSLOW and H. RAISTRICK (J.C.S., 1939, 1446–1457; cf. A., 1938, III, 443).—*p*-Benzoquinone and excess of NH_2Me in EtOH at room temp., then at 0° for 3 days, give 2 : 5-bismethylamino-1 : 4-benzoquinone (I), m.p. 284–286° (decomp.). Methoxy- or 2 : 5-dimethoxy-1 : 4-benzoquinone and boiling $NH_2Me-EtOH$ give (I). 2 : 6- or 2 : 3-Dimethoxy-1 : 4-benzoquinone in boiling or cold EtOH, respectively, affords 2 : 5-bismethylamino-3-methoxy-1 : 4-benzoquinone (II), m.p. 234°, hydrolysed by boiling 5N- H_2SO_4 to 2 : 5-dihydroxy-3-methoxy-1 : 4-benzoquinone (III), m.p. 159–160° (diacetate, m.p. 77°). *p*-Toluquinone or its 3- or 6-OMe- or 3 : 6-(OMe) $_2$ -derivative gives 3 : 6-bismethylamino-2 : 5-toluquinone, new m.p. 231° (cf. Fichter, A., 1908, i, 658). 4-Methoxy-2 : 5-toluquinone acts abnormally

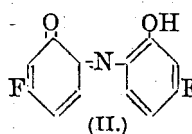


methoxyphenanthrene-1- β -propionic-2-carboxylic acid (IV), m.p. 285° (decomp.), with the condensation product (A), m.p. 301–302°, also obtained (solely) from (III) and $KOBu^+-Bu^+OH$ (under N_2) and $HCO_2C_5H_{11}$ -*iso*. The Me_2 ester, m.p. 115°, from (IV) and $MeOH-H_2SO_4$, purified chromatographically (Al_2O_3), is hydrogenated (PtO_2 in AcOH at 70°) and then hydrolysed (aq. $MeOH-KOH$) to three acids, regarded as 4 : 7-dimethoxy-9 : 10-dihydro- (V), m.p. 208–209°, and -1 : 2 : 3 : 4-tetrahydro- (VI),

and affords (I) (mechanism suggested), converted by boiling $2N$ -NaOH into 2:5-dihydroxy-1:4-benzoquinone (IV), and thence by aq. $Na_2S_2O_4$ into 1:2:4:5- $C_6H_2(OH)_4$, new m.p. 232—233° (some decomp. from 200°) (cf. Nietzki *et al.*, A., 1888, 1181). 3:4-Dimethoxy- or 3:4:6-trimethoxy-2:5-toluquinone (V), m.p. 80°, and NH_2Me -EtOH give 3:6-bismethylamino-4-methoxy-2:5-toluquinone, m.p. 231° (partial sublimation), hydrolysed by boiling $2N$ - H_2SO_4 to 3:6-dihydroxy-4-methoxy-2:5-toluquinone [spinulosin] (VI) [boiling NH_2Me -EtOH gives only the $(NH_2Me)_2$ salt, m.p. 173° (decomp. from 164°)]. (VI) and CH_2N_2 give (V), also formed in smaller yield using Me_2SO_4 - K_2CO_3 - $COMe_2$. 4:6-Dimethoxy-2:5-toluquinone acts abnormally with NH_2Me , giving (II) (mechanism suggested). (V) and aq. $Na_2S_2O_4$ give 2:5-dihydroxy-3:4:6-trimethoxytoluene, m.p. 82—83°. 1:2:4:5- $C_6H_2(OAc)_3$ OMe and boiling H_2SO_4 -MeOH (in N_2) give the quinol, oxidised (air at p_H 8) to 2-hydroxy-5-methoxy-1:4-benzoquinone (VII), m.p. 179° (decomp.) (darkens and softens from 171°) (2-acetate, m.p. 124°), converted by aq. $Na_2S_2O_4$ into 1:2:4-trihydroxy-5-methoxybenzene, m.p. 133°. (VII) and boiling NH_2Me -EtOH, then at room temp., give (I) and (?) 4:5-bismethylamino-1:2-benzoquinone, m.p. >360°, hydrolysed by $2N$ -NaOH to (IV). (VII) reacts possibly in the *o*-quinonoid form. 2:3-Dimethoxy-quinol and aq. $FeCl_3$ give the -quinone, converted by Ac_2O - H_2SO_4 into 2:3:1:4:5-(OMe) $_5C_6H(OAc)_3$, and thence [as for (VII)] into 5-hydroxy-2:3-dimethoxy-1:4-benzoquinone, m.p. 125—126° (softens at 115°) (1:4:5-trihydroxy-2:3-dimethoxybenzene has m.p. 157—158°). The latter and cold NH_2Me -EtOH give the NH_2Me salt, m.p. 228—230° (decomp.), of 2-methylamino-5-hydroxy-3-methoxy-1:4-benzoquinone [0.1N-HCl gives the free quinone, m.p. 179° (decomp.)], hydrolysed by boiling $5N$ - H_2SO_4 to (III). 2:5-Dihydroxy-3-methoxy-1:4-benzoquinone and cold NH_2Me -EtOH give the $(NH_2Me)_2$ salt, m.p. 214° (decomp.). 3-(fumigatin) or 6-hydroxy-4-methoxy-2:5-toluquinone (acts in *o*-quinonoid form) gives 6-methylamino-3-hydroxy-4-methoxy-2:5-, m.p. 213—214°, or (?) 5:6-bismethylamino-4-methoxy-2:3-toluquinone, m.p. 228°, respectively, both being hydrolysed by boiling aq. H_2SO_4 to (VI). 3-Methoxy-2:5-toluquinone and Ac_2O - H_2SO_4 give 2:5:6-triacetoxy-3-methoxytoluene, m.p. 155°, and thence [as for (VII)] 6-hydroxy-3-methoxy-2:5-toluquinone, m.p. 155—156° [6-acetate, m.p. 109°; 3:6-dimethoxytoluquinone, new m.p. 112° (cf. A., 1938, II, 237); 2:5:6-trihydroxy-3-methoxytoluene, m.p. 102—103°], converted by NH_2Me -EtOH (warm) into 3-methylamino-6-hydroxy-2:5-toluquinone, m.p. 252—254° (fumes from 220°), which is hydrolysed by boiling $2N$ -NaOH to 3:6-dihydroxy-2:5-toluquinone. 3:4-Dimethoxy-2:5-toluquinone and Ac_2O - H_2SO_4 , and then H_2SO_4 -MeOH (in N_2), give 2:5:6-trihydroxy-3:4-dimethoxytoluene, oxidised (air) to 6-hydroxy-3:4-dimethoxy-2:5-toluquinone, m.p. 105° (2:5:6-trihydroxy-3:4-dimethoxytoluene, m.p. 110—111°), which affords 3-methylamino-6-hydroxy-4-methoxy-2:5-toluquinone, m.p. 212—213°, hydrolysed by $2N$ - H_2SO_4 to (VI). No pure compound is isolated from 4-hydroxy-6-methoxy-2:5-toluquinone. In the cases where 2 OMe are replaced by 2 NHMe, yields

were ~100%, where 1 OMe is replaced, 50%, and with *p*-benzo- and tolu-quinone, 33%. A. T. P.

Nitrosation of phenols. XVI. *m*-Fluorophenol. A new red indophenol. H. H. HODGSON and D. E. NICHOLSON (J.C.S., 1939, 1405—1408).—*m*- C_6H_4F ·OH (I) does not give a NO-compound (cf. A., 1930, 1281), but in 50% aq. AcOH with aq. $NaNO_2$ (or in aq. NaOH- $NaNO_2$ followed by dil. H_2SO_4) gives red-brown *mm'*-difluoro-*o*-indophenol (II), no. m.p., which gives no steam-volatile org.

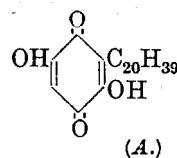


products when boiled with alkalis, $KMnO_4$, $K_3Fe(CN)_6$, or HNO_3 , and is sol. in cold aq. Na_2CO_3 , and in conc. H_2SO_4 to a red solution.

Other colour reactions supporting structure (II) include the formation of a red product from 2:5:1-NO- $C_6H_3(OMe)$ ·OH (III) and (I), and reduction of (II) (Zn-AcOH) to a leuco-compound, converted (O_2 + HCl) into a blue solution (oxazine) turned red by $FeCl_3$ [cf. indophenols from (III) and *p*-cresol or *p*- C_6H_4Cl ·OH]. The reaction of (I) and HNO_2 probably consists of slow 6-nitrosation (in this position because of powerful negative inductive effect of F on the 4-position), with some nitration [some 2:5:1-NO $_2$ - C_6H_3F ·OH is always formed with (II)], followed by rapid condensation of the product with (I) (cf. Schoutissen, A., 1922, i, 135).

E. W. W.

Maesaquinone, a pigment from the fruits of *Maesa japonica*. M. IIRAMOTO (Proc. Imp. Acad. Tokyo, 1939, 15, 220—222).—Extraction of the fruits with EtOH gives the orange-red *maesaquinone* (I), $C_{26}H_{42}O_4$, m.p. 122°, which is optically inactive and free from OMe but contains 2 OH since it yields a liquid Me_2 ether which solidifies when cooled and a diacetate, m.p. 45°. (I) dissolves in dil. alkali to a violet solution from which cryst. alkali salts are obtained. Zn and HCl in EtOH decolorise (I) but the colour returns on exposure to air. Reductive acetylation (Zn dust- Ac_2O) of (I) gives *leucomaesaquinone tetra-acetate*, m.p. 101.5°, catalytically hydrogenated to its H_2 -compound, m.p. 121°, thus establishing the presence of a double linking in the side-chain. Under similar conditions (I) absorbs 2 H_2 and the quinol thus produced becomes coloured on exposure to air with formation of *dihydromaesaquinone*, m.p. 134° (diacetate, m.p. 90°; Me_2 ether, m.p. 75°), oxidised by H_2O_2 and alkali or by $KMnO_4$ to heneicosanoic acid. The close relationship of *Maesa* and *Embelia* appears to justify the consideration of (I) as a higher homologue of embelin (II) and thus to be



(A), whereby the position of the double linking in the side-chain remains obscure. Difficulties in interpreting the course of the oxidation of (II) are discussed.

H. W.

Synthesis of phthiocol. R. J. ANDERSON and M. M. CREIGHTON (J. Biol. Chem., 1939, 130, 429—430).—2- $C_{10}H_7Me$ is treated successively with CrO_3 , aq. $Ca(OCl)_2$, and 25% (vol.) H_2SO_4 at 100°, thus giving 57% of phthiocol.

R. S. C.

Syntheses of hydroxydroserone (the pigment of *Drosera whittakeri*), phthiocol (the pigment of

human tubercle bacillus), and naphthapurpurin; studies of related compounds. C. KURODA (Proc. Imp. Acad. Tokyo, 1939, 15, 226—229).—Naphthazarin (I) and all naphthaquinones which do not contain OH in the β position of the quinone ring do not react with NaHCO_3 whereas naphthapurpurin (II) and naphthaquinones containing β -OH react with NaHCO_3 and with the Na salts of certain weak acids; e.g., AcOH . This behaviour is useful in separating compounds of the two classes. Na_3 derivatives of 2:5:8-trihydroxy- (III), 2:5:8-trihydroxy-6- or -7-methyl- (IV), 2:5:8-trihydroxy-3-methyl- (V), and 2-hydroxy-1:4-naphthaquinone are described. (II) is obtained by heating a solution of (I) in 0.5% aq. NaOH at 100° in contact with air, using a mechanical stirrer, and is separated from any unchanged (I) by NaHCO_3 . The H of the OH in β position of the quinone ring can be replaced by Me by MeOH-HCl ; thus are obtained the 2-Me ethers, m.p. 178° and —, of (III) and (IV); (V) does not react. Rapanone similarly gives a Na compound and a Me_1 ether, m.p. 95° , whereas a Me_2 ether is produced with CH_2N_2 . 5:8-Dihydroxy-2-methyl-1:4-naphthaquinone, obtained from maleic acid and toluquinol, or from citraconic acid and quinol, is transformed by air and 0.5% NaOH into (V) (hydroxydrosone), m.p. 198° (Ac derivative, m.p. 152°). $2\text{-C}_{10}\text{H}_7\text{Me}$ is oxidised by CrO_3 to 2-methyl-1:4-naphthaquinone, which is converted by 0.5% NaOH into phthiocol, m.p. 173° (Ac_1 derivative, m.p. 106°), transformed by Zn , Ac_2O , and NaOAc into $\text{C}_{10}\text{H}_4\text{Me}(\text{OAc})_3$, m.p. 158° . Maleic anhydride, 1:4:2:3-(OH) $_2$ $\text{C}_6\text{H}_2(\text{OMe})_2$, AlCl_3 , and NaCl give 2:3:5:8-tetrahydroxy-1:4-naphthaquinone, m.p. 270° . Citraconic anhydride and 2:1:4- $\text{C}_6\text{H}_3\text{Me}(\text{OH})_2$ yield 5:8-dihydroxy-2:6- and -2:7-dimethyl-1:4-naphthaquinone, m.p. 127° and 215° .

H. W.

Synthesis of quinones related to vitamins- K_1 and - K_2 . L. F. FIESER, W. P. CAMPBELL, and E. M. FRY (J. Amer. Chem. Soc., 1939, 61, 2206—2218).—Partly a detailed account of work already reported (A., 1939, II, 432). The structural arguments are expanded and the biological results modified in view of unreliability of the rapid Ansbacher technique (-K-activity) for pure substances. The following are new. 4:2:1- $p\text{-SO}_3\text{H-C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ and $\text{Na}_2\text{S}_2\text{O}_4$ etc. give 4-amino-2-allyl-1-naphthol hydrochloride (I). 2-Allyl-1:4-naphthaquinone (colour reactions described) with $\text{H}_2\text{O}_2\text{-KOH-aq. EtOH}$ gives 2-hydroxy-1:4-naphthaquinone, this fission being the basis of the Dam colour reaction. $\text{H}_2\text{-PtO}_2$ reduces (I) in H_2O to a cryst. hydrochloride, converted by FeCl_3 into 2-n-propyl-1:4-naphthaquinone, m.p. $39\text{--}39.5^\circ$, which is obtained also from the allyl-quinone by hydrogenation in EtOH and subsequent Ag_2O oxidation. 2:3-Diallyl-1:4-naphthaquinone and $\text{KOH-EtOH-H}_2\text{O}$ give 2-hydroxy-3-allyl-1:4-naphthaquinone. Quinol diallyl ether in boiling kerosene (N_2) gives 2:3-, m.p. $87\text{--}90^\circ$, and 2:5-diallylquinol (29%), m.p. $129.5\text{--}131^\circ$, oxidised (Ag_2O) to the quinones, an oil and m.p. 16° , respectively. $p\text{-O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ and $(\text{CH}_2\cdot\text{CMe})_2$ in C_6H_6 give a substance, m.p. $113\text{--}115^\circ$, isomerised by N-alkali in N_2 to 1:4-dihydroxy-6:7-dimethyl-5:8-dihydronaphthalene, m.p. $232\text{--}238^\circ$, which with CrO_3 affords first a

product, $(\text{C}_{12}\text{H}_{11}\text{O}_2)_x$, m.p. $120\text{--}126^\circ$ (decomp.), and then the 6:7-dimethyl-1:4-naphthaquinone. 6:7-Dimethyl-2:3-diallyl-5:8-dihydro-1:4-naphthaquinol, m.p. $156.5\text{--}159^\circ$, and CrO_3 at 60° similarly give a compound, $(\text{C}_{18}\text{H}_{19}\text{O}_2)_x$, m.p. $54\text{--}56^\circ$ after sintering, and thence at $80\text{--}100^\circ$ 6:7-dimethyl-2:3-diallyl-1:4-naphthaquinone. 4-Amino-3:7-dimethyl-2-allyl-1-naphthol hydrochloride, $+3\text{H}_2\text{O}$, cryst., and the absorption spectra of 2:3-dimethyl-, 2:6-dimethyl-3-allyl-, 6:7-dimethyl-2:3-diallyl-, and 2:3-diallyl-1:4-naphthaquinone are described.

R. S. C.

Constitution and synthesis of vitamin- K_1 . S. B. BINKLEY, L. C. CHENEY, W. F. HOLCOMB, R. W. MCKEE, S. A. THAYER, D. W. MCCORQUODALE, and E. A. DOISY (J. Amer. Chem. Soc., 1939, 61, 2558—2559).— $\zeta\kappa$ -Trimethylpentadecan- β -one, obtained (A., 1939, II, 433) from vitamin- K_1 , is identified by mixed m.p. The quinone-acid (*loc. cit.*) thought to be 2-ethyl-, is shown to be 2-methyl-1:4-naphthaquinonyl-3-acetic acid (I) (*Me* ester, m.p. $121.5\text{--}122.5^\circ$). Dihydrovitamin- K_1 diacetate (II) and CrO_3 give 1:4-diacetoxy-2-methyl-3-naphthylacetic acid, m.p. 205° (*Me* ester, m.p. $127.5\text{--}128.5^\circ$, synthesised), further oxidised to (I). The Na_1 salt of 2:1:4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OH})_2$ and phytol bromide in C_6H_6 give a quinol, oxidised by air to a quinone [purified by adsorption and distillation (high vac.)], reductive acetylation of which affords (II). $-K_1$ is thus 2-methyl-3-phytyl-1:4-naphthaquinone. R. S. C.

(A) **Synthetic approach to vitamin- K_1 .** L. F. FIESER, W. P. CAMPBELL, E. M. FRY, and M. D. GATES, jun. (B) **Synthesis of 2-methyl-3-phytyl-1:4-naphthaquinone.** (C) **Identity of synthetic 2-methyl-3-phytyl-1:4-naphthaquinone and vitamin- K_1 .** L. F. FIESER (J. Amer. Chem. Soc., 1939, 61, 2559, 2559—2561, 2561).—(A) In presence of anhyd. $\text{H}_2\text{C}_2\text{O}_4$, 2:1:4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OH})_2$ condenses (in boiling dioxan) with β -unsaturated alcohols or dienes. With $(\text{CH}_2\cdot\text{CMe})_2$ it gives 1:4-dihydroxy-2-methyl-3- β -dimethyl- Δ^2 -butenyl-naphthalene (I) (29%) [diacetate (II), m.p. $119\text{--}120^\circ$], and a substance (13%), m.p. $73\text{--}73.5^\circ$, of tocopherol type. Oxidation of (I) gives 2-methyl-3- β -dimethyl- Δ^2 -butenyl-1:4-naphthaquinone, m.p. $95\text{--}95.5^\circ$, reduced by Zn dust in $\text{C}_5\text{H}_5\text{N-Ac}_2\text{O}$ to (II). $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ similarly gives a quinol (diacetate, m.p. $167.5\text{--}168^\circ$) and a quinone, m.p. $127\text{--}127.5^\circ$. Phytol (as above or at 140°) affords probably the tocopherol. An acetoxyquinone, $\text{C}_{23}\text{H}_{28}\text{O}_4$, was obtained in the geranyl series by a similar reaction, followed by $\text{Pb}(\text{OAc})_4$ -oxidation. Addition of Grignard reagents to 2-alkyl-1:4-naphthaquinone oxides (prep. by H_2O_2 in $\text{Na}_2\text{CO}_3\text{-EtOH-H}_2\text{O}$) is not promising. 2:6-Dimethyl-1:4-naphthaquinone oxide, m.p. $97\text{--}98^\circ$, with $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$ or MgBr_2 in Et $_2\text{O}$ gives a bromohydrin, m.p. $146\text{--}148^\circ$ (derived bromodimethylnaphthaquinone, m.p. $114\text{--}114.7^\circ$).

(B) 2:1:4- $\text{C}_{10}\text{H}_5\text{Me}(\text{OH})_2$ and phytol in dioxan with $\text{H}_2\text{C}_2\text{O}_4$ or $\text{CCl}_3\cdot\text{CO}_2\text{H}$ at 75° give a quinol, oxidised to 2-methyl-3-phytyl-1:4-naphthaquinone (III), an oil, which has the absorption spectrum and physiological activity of vitamin- K_1 and gives similar derivatives (quinol diacetate and dibenzoate, m.p. $85\text{--}86^\circ$). 2:6-Dimethyl-3-phytyl- and 2-methyl-3-

geranyl-1:4-naphthaquinone have been similarly prepared.

(c) Identity of (III) and $-K_1$ is established by direct comparison of chemical, physical, and biological properties. R. S. C.

Photo-reactions. IV. Photo-reaction between phenanthraquinone and aromatic aldehydes. A new passage from phenanthraquinone to fluorenone. A. SCHÖNBERG and R. MOUBACHER (J.C.S., 1939, 1430—1432; cf. A., 1936, 437).—Phenanthraquinone (I) and PhCHO or p -C₆H₄Cl·CHO in sunlight give 9:10-dihydroxyphenanthrene α -hydroxybenzylidene (II), m.p. 177—178°, or α -hydroxy- p -chlorobenzylidene ether (III), m.p. \sim 222° (decomp.), respectively (cf. Klinger, A., 1889, 405); p -OMe·C₆H₄·CHO reacts similarly. (II) is converted by HNO₃ (d 1.3) at 90° into (I). (II) and (III) are methylated (CH₃N₂) to the α -OMe-derivatives, m.p. 80° (IV) and 170°, respectively. The latter is hydrolysed (20% aq. NaOH at 40°) to p -C₆H₄Cl·CO₂Me and 9:10-dihydroxyphenanthrene [aëration gives (I)]; (IV) similarly gives (I). Pyrolysis of (II) at 200° in vac. affords fluorenone (probably via diphenyleneketen) and BzOH, with some (I) and PhCHO. Similar decomp. of α -stilbenediol diacetate (modified prep.) at 165° gives Bz₂. A. T. P.

Derivatives of 1:2-benzanthraquinone-4'-sulphonic acid. A. SEMPRONJ (Gazzetta, 1939, 69, 448—453).—Sulphonation (method: Heller *et al.*, A., 1908, i, 994) of 1:2-benzanthraquinone gives the 4'-sulphonic acid; the K salt (I), with KOH at 260° gives BzOH and 5:2-OH·C₁₀H₆·CO₂H. The 4'-sulphonyl chloride, m.p. 263°, at 275° yields 4'-chloro-1:2-benzanthraquinone (cf. Johnson *et al.*, A., 1932, 1030), also obtained from (I) and NaClO₃ in conc. HCl at the b.p. Reduction (Zn-aq. NH₃) of (I) gives 1:2-benzanthracene-4'-sulphonic acid (II) (chloride, m.p. 193°; Et ester, m.p. 157°), which with KOH at 300° yields 4'-hydroxy-1:2-benzanthracene, m.p. 230° (Me ether, m.p. 163°). The corresponding 4'-acetoxy-derivative, m.p. 193—194°, is oxidised (K₂Cr₂O₇-AcOH) to 4'-acetoxy-1:2-benzanthraquinone, m.p. 202—203°, hydrolysed to the 4'-OH-compound, m.p. 224—225°. The K salt of (II) distilled with KCN gives 1:2-benzanthracene. E. W. W.

1-Nitrosomenthoneoxime and its decomposition. J. C. EARL, D. JOHNSON, and J. G. MCKEAN (J. Proc. Roy. Soc. New South Wales, 1939, 72, 109—112).—Piperitone hydroxylamino-oxime is oxidised by yellow HgO in boiling CHCl₃ to 1-nitrosomenthoneoxime, m.p. 124—125° to a blue liquid; this passes when kept or heated into N₂O and piperitoneoxime. H. W.

Addition of oxygen to double linkings. S. TANAKA (Mem. Coll. Sci. Kyoto, 1939, 22, A, 97—197).— Δ^3 - p -Menthene (I) and BzO₂H or AcO₂H in CHCl₃ or Et₂O give menthene 3:4-oxide (II), b.p. 74—75°/14 mm., probably by decomp. of an intermediate unstable ester. (II) and 10% aq. H₂SO₄ at 0° give the 3:4-glycol, m.p. 75—76°, converted by 10% aq. H₂SO₄ at 100° into i -menthone, also obtained by passing (II) over Al₂O₃ at 250°. (I) and HOCl or HOI give the chloro- or iodo-hydrin (III), respect-

ively, converted by KOH into (II), also obtained from (III) and AgOBz or AgOAc in 80% EtOH at 100°. Stilbene and AcO₂H give the oxide; in CHCl₃, 94% of α - and 6% of β -oxide in 19.5 hr.; in Et₂O, 100% of α in 200 hr. The mechanism of oxidation of PhCHO and MeCHO, by BzO₂H or AcO₂H, involving formation of intermediate additive compound, is discussed. Oxidation velocities of (I), β - γ -dimethyl- Δ^4 -octene, styrene, heptaldehyde, and PhCHO with AcO₂H are compared; the speed with C:C is $>$ with C:O derivatives. The biological connexion of the results is discussed. A. T. P.

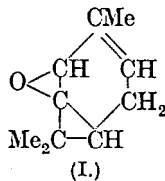
Catalytic action of Japanese acid clay on terpene compounds. VI. Hydration of limonene with acetic acid. T. KUWATA (J. Soc. Chem. Ind. Japan, 1939, 42, 247B).—In presence of activated Japanese acid clay, an equimol. mixture of d -limonene (I) and AcOH gives 35—40% of d - α -terpinyl acetate. When reaction is effected at 15—25° the proportion of polymerised substances is small, most of the unused (I) being recovered unchanged. H. W.

Phellandrene nitrosites. II. α - and β -Nitrosite of d - α -phellandrene. P. A. BERRY, A. K. MACBETH, and T. B. SWANSON (J.C.S., 1939, 1418—1421).— d - α -Phellandrene α -, m.p. 119°, $[\alpha]_D^{20}$ -133.8° in CHCl₃, and β -nitrosite, m.p. 100°, $[\alpha]_D^{20}$ +198.3° in CHCl₃, have been prepared (cf. A., 1939, II, 220). The mutarotations of the compounds and transmutation of the β - into the α -nitrosite have been examined. F. R. S.

1- Δ^3 -Carene 5:6-epoxide, a constituent of the oil from *Zieria Smithii*. A. R. PENFOLD, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1939, 1496—1504).—From the oil there have been isolated linalool (*xenylurethane*, m.p. 83—85°), an alcohol, C₁₀H₁₄O (3:5-dinitrobenzoate, m.p. 119°), and 1- Δ^3 -carene 5:6-epoxide (I), C₁₀H₁₄O, b.p. 83—85°/14 mm., $[\alpha]_{4461}^{20}$ -88°. Ozonolysis of (I) gives *cis*-homocaronic acid (*di-p*-phenacyl ester, m.p. 147—149°), with some COMe₂, CH₂O, and *trans*-caronic acid (?). With hot aq. KOH, (I) affords geranic acid, but with cold EtOH-KOH, a mixture is obtained, from which can be separated an acid, C₁₀H₁₆O₂, m.p. 83° (an active Δ^2 -cyclogeranic acid?). The action of HCl and HBr on (I) yields respectively dl-1:8-dichloro-, decomp. 72°, and -dibromo- p -menthan-3-one (II), decomp. 74°, which is hydrogenated (Pd-C) to *dl*-menthone (2:4-dinitrophenylhydrazone, m.p. 141—142°). The foregoing reactions are in accord with the suggested structure.

When (I) is heated at 160—165°, an oil is formed which gives a 2:4-dinitrophenylhydrazone, m.p. 218—220°, and a mixture of semicarbazones, from which an α -, decomp. 221—222°, and β -semicarbazone, decomp. 183—185°, can be separated.

Certain observations do not eliminate the possibility that (I) is a bicyclic ketone with a somewhat inert CO. Semicarbazide acetate and (I) in the cold for several days afford a semicarbazone, m.p. 192°, $[\alpha]_{4461}^{20}$ -95° in C₅H₅N, derived from C₁₀H₁₄O, but not homogeneous; it is hydrogenated to a mixture from which can be separated a semicarbazone, m.p. 212°, and is hydro-



lysed [steam- α -C₆H₄(CO₂H)₂] to a mixture containing a fraction, C₇H₁₀O, b.p. 87°/15 mm., $[\alpha]_{5161} +26.3^\circ$ (2 : 4-dinitrophenylhydrazine, m.p. 176°, not identical with the corresponding derivative from 2-methyl- Δ^2 -cyclohexenone, m.p. 202—203°, or the 3-Me compound), and a fraction, b.p. 127—130°/13 mm., $[\alpha]_{5161} +6.52^\circ$ (a mixture containing $\Delta^{1.4(8)}$ -p-menthadien-3-one). These results do not agree with a ketonic structure for (I). Alcoholic 2 : 4-dinitrophenylhydrazine sulphate with (I) gives an α -, m.p. 192—193°, and β -2 : 4-dinitrophenylhydrazine, C₁₈H₂₄O₅N₄, m.p. 165—166°, whilst the aq. reagent affords a 2 : 4-dinitrophenylhydrazine, C₁₆H₂₀O₅N₄, m.p. 145—147°. NaOAc-AcOH and (II) give $\Delta^{1.4(8)}$ -p-menthadien-3-one, b.p. 120—122°/14 mm., $[\alpha]_{5161} -0.1^\circ$ (2 : 4-dinitrophenylhydrazine, α -form, m.p. 187°, β -form, m.p. 125—127°), which on ozonolysis affords COMe₂, lævulic acid, an oil (semicarbazone, decomp. 232—233°), and β -methyl- Δ^2 -butene- $\alpha\delta$ -dicarboxylic acid, m.p. 140—141°, the latter reduced to β -methyladipic acid (di-p-phenylphenacyl ester, m.p. 124—125°). F. R. S.

Thujone series. III. Sabina ketone. A. G. SHORT and J. READ (J.C.S., 1939, 1415—1418).—Oxidation of sabinene with KMnO₄ gives crude l-sabina ketone (I), which is reduced (Na-EtOH) to a mixture of ketols, b.p. 96—101°/15 mm., $\alpha_D^{25} +65.00^\circ$ ($l = 1$) and b.p. 126—132°/0.5 mm., $\alpha_D^{25} +50.50^\circ$ ($l = 1$). The former fraction and p-NO₂-C₆H₄-COCl afford d- α -sabinaketyl p-nitrobenzoate, m.p. 89.5°, $[\alpha]_D^{25} +94.5^\circ$ in CHCl₃, hydrolysed to d- α -sabina ketol, b.p. 100°/16 mm., $\alpha_D^{25} +88.84^\circ$ ($l = 1$), $[\alpha]_D^{25} +90.6^\circ$ in EtOH. Oxidation (CrO₃) of this ketol yields pure (I), b.p. 97.5°/17 mm., $[\alpha]_D^{25} -34.2^\circ$ in EtOH (2 : 4-dinitrophenylhydrazine, m.p. 124.5°, $[\alpha]_D^{25} +135.2^\circ$ in CHCl₃). Amination (HCO₂NH₄) of crude (I) gives a ketylamine, b.p. 63—64°/19.5 mm., $\alpha_D^{25} +43.8^\circ$ ($l = 1$), probably a mixture, and disabinaketylamine, b.p. 166—167°/9.5 mm., $[\alpha]_D^{25} +60.6^\circ$ in CHCl₃; from the mixture a p-nitrobenzoylsabinaketylamine, m.p. 141°, $[\alpha]_D^{25} +84.0^\circ$ in CHCl₃, has been prepared. Some of the structural and stereochemical relationships of (I) are discussed. F. R. S.

Terpenoid amines. I. Isomeric α -thujylamines. H. L. DICKSON and A. W. INGERSOLL (J. Amer. Chem. Soc., 1939, 61, 2477—2482).—Thujylamines are named by reference (α , β) to the thujone to which they are related and by assigning the prefix *iso* to that member of a pair having the higher numerical α . The most characteristic salts are marked * below. When impure α -thujone (from *Thuja occidentalis*), $\alpha_D^{25} -18^\circ$, and HCO₂NH₄ are heated with separation of the aq. (NH₄)₂CO₃ formed and are then heated at 175—185°, there are formed (+)- β - (I), b.p. 199.6°/750 mm., 77.0°/12 mm., $\alpha +27.8^\circ$ (homogeneous), $[\alpha] +51.27^\circ$ in EtOH, $+35.31^\circ$ in C₆H₆ [Bz derivative, m.p. 73—75°, $[\alpha] +91.44^\circ$ in MeOH; sulphate*, m.p. 242° (decomp.), $[\alpha] +42.77^\circ$; p-toluenesulphonate*, m.p. 194.7°, $[\alpha] +27.91^\circ$; H oxalate, +H₂O, $[\alpha] +36.10^\circ$ (anhyd.); nitrate, +0.5H₂O, m.p. 105°, $[\alpha] +35.97^\circ$; d-, +2H₂O, m.p. 80—113°, $[\alpha] +82.59^\circ$, and l-mandelate, +H₂O, m.p. 120—128°, $[\alpha] -29.52^\circ$, (+)-iso- β - (II), b.p.

193.4°/737 mm., 76.8°/11 mm., $\alpha +94.94^\circ$ (homogeneous), $[\alpha] +107.9^\circ$ in EtOH, $+108.4^\circ$ in C₆H₆ [Bz derivative, m.p. 131.5°, $[\alpha] +87.74^\circ$ in MeOH, $+90.5^\circ$ in CHCl₃; H sulphate, +H₂O, m.p. 153° (decomp.), $[\alpha] +55.25^\circ$; p-toluenesulphonate, m.p. 170—171°, $[\alpha] +41.6^\circ$; H oxalate*, +H₂O, m.p. 167°, $[\alpha] +62.50^\circ$ (anhyd.); nitrate*, m.p. 176.9°, $[\alpha] +70.48^\circ$; ?-malate, m.p. 160°, $[\alpha] +49.84^\circ$; perchlorate, m.p. 168°, $[\alpha] +55.47^\circ$, (—)- α - (II), b.p. 196.7°/756 mm., 77.6°/12 mm., $\alpha -14.15^\circ$ (homogeneous), $[\alpha] -1.41^\circ$ in EtOH, -13.25° in C₆H₆ [Bz derivative, m.p. 94.5°, $[\alpha] -12.16^\circ$ in C₆H₆; sulphate*, +4H₂O, m.p. 243° (decomp.), $[\alpha] +3.47^\circ$ (anhyd.); p-toluenesulphonate, a glass; oxalate*, m.p. 200—201°; nitrate, m.p. 150°, $[\alpha] +2.60^\circ$; H dl-malate, m.p. 148.5°, $[\alpha] +1.73^\circ$; d-mandelate, +H₂O, m.p. 99.5°, $[\alpha] +65.23^\circ$, (—)-iso- α -thujylamine (IV), b.p. 202.2°/748 mm., 81.1°/12 mm., $\alpha_D^{25} -22.07^\circ$ (homogeneous), $[\alpha]_D^{25} -23.29^\circ$ in EtOH, -26.92° in C₆H₆ [Bz, a glass, and p-nitrobenzoyl derivative, m.p. 146.5°, $[\alpha] -51.25^\circ$ in CHCl₃; sulphate*, +H₂O, m.p. 263° (decomp.), $[\alpha] -16.66^\circ$ (anhyd.); p-toluenesulphonate, m.p. 198.6°, $[\alpha] -10.40^\circ$; oxalate, m.p. 235° (decomp.), $[\alpha] -12.37^\circ$; nitrate, m.p. 159—160°, $[\alpha] -15.18^\circ$; H l-malate, m.p. 186—187°, $[\alpha] -14.73^\circ$, and (+)-fenchylamine (from the fenchone present in the ketone), b.p. 195.3°/730 mm., 73.4°/11.5 mm., $\alpha_D^{25} +22.19^\circ$ (homogeneous), $[\alpha]_D^{25} +25.89^\circ$ in EtOH, $+19.11^\circ$ in C₆H₆ [Bz derivative, m.p. 90.2°, $[\alpha] +24.43^\circ$ in MeOH; sulphate; p-toluenesulphonate, +H₂O, m.p. 188—189°, $[\alpha] +2.60^\circ$ (anhyd.); H oxalate, m.p. 165°, $[\alpha] +3.11^\circ$; nitrate, +0.5H₂O, m.p. 190° (decomp.), $[\alpha] +3.41^\circ$ (anhyd.); H l-malate*, m.p. 191—193°, $[\alpha] 0$; d-mandelate*, m.p. 190.3°, $[\alpha] +60.8^\circ$. β -Thujoneoxime, m.p. 53° $[\alpha] +105.3^\circ$ in MeOH, and Na-EtOH give 83.7% of (II), 6% of (I), 4% of (IV), and a trace of (III) [cf. Short *et al.*, A., 1939, II, 79; d-isothujylamine = (II); their l-thujylamine = (IV)]. dl-Mandelic acid is readily resolved by (I), (III), or (V), and dl-malic acid by (IV) or (V). Unless otherwise stated, $[\alpha]$ are $[\alpha]_D^{25}$ in H₂O (for the salts, including any H₂O of crystallisation).

R. S. C.

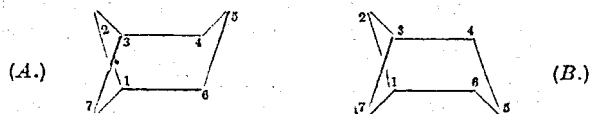
Structure of origanene. II. Its identity with α -thujene. A. J. BIRCH and J. C. EARL (J. Proc. Roy. Soc. New South Wales, 1939, 72, 55—61; cf. A., 1939, II, 170).—Origanene (I), obtained from oil of *Eucalyptus dives*, is a mixture of d- and dl- α -thujene. The latter gives a characteristic nitrosochloride apparently identical with that obtained from (I). Oxidation of (I) by KMnO₄ in COMe₂ yields the cryst. α -thujaketonic acid (II), m.p. 75—76°, $[\alpha]_D -200^\circ$ in H₂O, and a liquid acid, probably mainly dl- α -thujaketonic acid (III), which yields a semicarbazone, m.p. 196—197°; a little d-pinonic acid appears to be present. Distillation of (II) or (III) under reduced pressure affords β -thujaketonic acid, identified by comparison with an authentic specimen and by oxidation to β -tanacetogendicarboxylic acid. The identity of (I) with α -thujene is confirmed by the conversion of the dibromide into p-cymene by C₅H₅N and by the production of terpinene dihydrochloride by the action of HCl in AcOH.

H. W.

Oximino- α -thujene. A. J. BIRCH (J. Proc. Roy. Soc. New South Wales, 1939, 72, 106—108).— α -Thujene nitroschloride is transformed by hot aq. C_5H_5N into *oximino- α -thujene* (I), which could not be cryst. or distilled. This is transformed into 1 : 3 : 2- $C_6H_3MePr^b \cdot NH \cdot OH$ (II) (*hydrochloride*, m.p. 149°) by the short action of cold, conc. HCl. (I) or (II) is converted by hot conc. HCl into 1 : 3 : 5 : 2- $C_6H_2MePr^bCl \cdot NH_2$ (III) and by 50% H_2SO_4 into *p*-aminothymol. This can be obtained exactly similarly from carvoxime but it has not been found possible to prepare (III) by the action of conc. HCl on the latter since hydrolysis occurs with ultimate formation of carvacrol. H. W.

Action of acetic acid on camphene in the presence of boric acid or boric trioxide. Action of acetic acid on camphene in the presence of boric acid. M. IMOTO (J. Soc. Chem. Ind. Japan, 1939, 42, 230—232B; cf. A., 1938, II, 416).—When heated at 110—120° for about 46 hr. camphene (I) and glacial AcOH give only 12.4% of ester. (I), AcOH, and H_3BO_3 afford 1.6% of ester in 7 hr. at 95—98° and 3.4% in 8 hr. at 110—120°; addition of H_2O to the mixture has little effect. (I), AcOH, and B_2O_3 give little ester at room temp. or at 50—60°; the yield is 32.0% when the reactant ratio is 1.5 : 2 : 0.67 (32 hr.) and 20.7% with 1 : 1.5 : 0.1 (24 hr.); the ester produced is *isobornyl acetate* (II), b.p. 95°/15 mm., $[\alpha]_D^{25} -7.25^\circ$. Between (I), Ac_2O , and H_3BO_3 the reactions are: $3Ac_2O + H_3BO_3 = 3AcOH + B(OAc)_3$ and $3C_{10}H_{16} + 3AcOH = 3C_{10}H_{17} \cdot OAc$; the results obtained are better than those with α -pinene (*loc. cit.*). In both cases abrupt heating causes an explosive reaction so that it is necessary to drop the Ac_2O into the heated mixture of (I) and H_3BO_3 . The max. recorded yield of ester is 65.1%. The existence of an equilibrium $(I) + Ac_2O \rightleftharpoons (II)$ is established. H. W.

Stereochemistry of pinane and its derivatives. K. GANAPATHI (J. Indian Inst. Sci., 1939, 22, A, 155—169).—The norpinane (I) ring system can exist in the strainless forms (A) and (B). On the basis of these formulæ detailed consideration is given to the

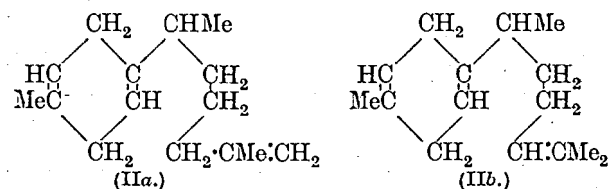


phenomena of isomerism between (I) and nopinane, among compounds substituted at $C_{(4)}$ or $C_{(5)}$, those substituted at two of the atoms 4, 5, or 6, those substituted at $C_{(2)}$ or $C_{(3)}$, and those with double linkings. The bearing of the space configuration on the stability of pinane and its derivatives, the isomerisation of β -to α -pinene, and on ring fission and isomerisation is discussed. H. W.

Constituents of some Indian essential oils. XXVI. Structures of *l*- α - and - β -curcumenes. F. D. CARTER, F. C. COPP, B. S. RAO, J. L. SIMONSEN, and (in part) K. S. SUBRAMANIAM (J.C.S., 1939, 1504—1509).—*l*- α -Curcumenol (I) (cf. A., 1928, 1253) with Se gives cadalene together with an azulene. 1-Dihydro- α -curcumenylamine, b.p. 153—154°/14 mm.

(Ac derivative, m.p. 109°), is converted by AcOH- $NaNO_2$ into (I). Oxidation of (I) with MnO_2 affords a mixture containing *p*- $C_6H_4Me \cdot CO_2H$, *p*- $C_6H_4(CO_2H)_2$, and 1 : 2 : 4- $C_6H_3(CO_2H)_3$, and with O_3 yields $COMe_2$, CH_2O , 1-8-*p*-tolylamyl Me ketone, b.p. 154°/15 mm., $[\alpha]_{5461} -30.8^\circ$ (*semicarbazone*, m.p. 138—139°), γ -*p*-tolylvaleraldehyde (2 : 4-dinitrophenylhydrazone, m.p. 94—95°), and 1- γ -*p*-tolyl-*n*-valeric acid, b.p. 180°/17 mm., $[\alpha]_{5461} -13.82^\circ$ in EtOH (*p*-phenylphenacyl ester, m.p. 73—74°). These results indicate that (I) is a mixture of 1- ζ -*p*-tolyl- β -methyl- Δ^b -heptene and Δ^a -heptene, the Δ^b -compound predominating in the natural hydrocarbon, with approx. equal quantities of Δ^a - and Δ^b -compounds in the hydrocarbon liberated from the hydrochloride.

l- β -Curcumenol (II) has been shown to be a mixture of two hydrocarbons (IIa and b). Ozonolysis of (II)



gives CH_2O , $COMe_2$, a diketone, $C_9H_{16}O_2$ (*di*-2 : 4-dinitrophenylhydrazone, m.p. 178—180°), together with small amounts of lactic acid and the degradation products of (I). Oxidation of (II) with SeO_2 affords 1- β -curcumenol, $C_{15}H_{22}O$, b.p. 149—150°/3 mm., $[\alpha]_{5461} -74.1^\circ$ (*semicarbazone*, m.p. 159°), $[\alpha]_D -77.8^\circ$ in $CHCl_3$; 2 : 4-dinitrophenylhydrazone, m.p. 139°, $[\alpha]_D -145.4^\circ$ in $CHCl_3$; nitroguanyllhydrazone, m.p. 151°, $[\alpha]_D -86.1^\circ$ in $CHCl_3$; oxime, b.p. 170—175°/4 mm., $[\alpha]_D -67^\circ$; β -curcumenonitrile, b.p. 178—182°/17 mm., and its anilide, m.p. 87°; Me ester, b.p. ~180—182°/16 mm., of β -curcumenylic acid, and 1- β -curcumenol, b.p. 175°/17 mm., $[\alpha]_D -39^\circ$ (*p*-xenyurethane, m.p. 79—80°). Ozonolysis of a mixture of (I) and (II) gives a keto-acid, oxidised ($NaOBr$) to α -methylglutaric acid.

From the lower-boiling hydrocarbon fraction of the oil from *C. aromatica*, there has also been isolated a hydrocarbon which contains a conjugated system, and from the higher-boiling fractions a black picrate, m.p. 120° (*s*-guajazulene picrate?). F. R. S.

Lignin and related compounds. XLI. Detection, isolation, and determination of the syringyl radical in plant products. M. J. HUNTER and H. HIBBERT. XLII. Isolation of a bisulphite-soluble "extracted lignin." W. H. STEEVES and H. HIBBERT. XLIII. Absence of the piperonyl group in the lignin structure. M. J. HUNTER and H. HIBBERT. XLIV. Ethanolysis of maple wood. Separation and identification of the water-soluble aldehyde constituents. J. J. PYLE, L. BRICKMAN, and H. HIBBERT (J. Amer. Chem. Soc., 1939, 61, 2190—2194, 2194—2195, 2196—2198, 2198—2203; cf. A., 1939, II, 382).—XLI. Syringyl, admixed with guaiacyl, derivatives containing CO *p*-to the OH are determined by pptg. the K salt of the former by KOAc in EtOH. Other less effective reagents are KOAc-EtOH-Et₂O > NH_3 -EtOH > NH_3 -Et₂O > KOH-EtOH. NH_3 in dry Et₂O ppts. salts of

both series. The phenolic fraction obtained by ethanolysis of maple wood is thus shown to contain 53% of 4:3:5:1-OH·C₆H₂(OMe)₂·CO·CHMe·OEt. Clemmensen reduction of propiosyringone gives 26.6% of 1:3:5:4-C₆H₂Pr^o(OMe)₂·OH. 4:3:5:1-OH·C₆H₂(OMe)₂·CO·CHMe·OAc and KOH-MeOH give 98% of a K salt, converted by AcOH into α -hydroxypropiosyringone, m.p. 126—127°.

XLII. Red oak meal is extracted successively with EtOH-C₆H₆, H₂O, 5% NaOH-N₂, H₂O, 1% AcOH, H₂O, and MeOH, and acetylated with Ac₂O-AcOH-H₂SO₄ at 15—30°. The product is purified to OMe 11.1% by fractional pptn. and then hydrolysed by NaOH in aq. CMe₂ to give a lignin (OMe 20.8%), which is sol. in aq. NaHSO₃ and is partly reacetylated by Ac₂O-C₆H₅N. Fructose and hydroxymethylfurfuraldehyde give cryst. acetylated products, which produce no lignin when hydrolysed.

XLIII. The CH₂O-producing component of maple and sassafras lignin is almost entirely removed by heating with 95% HCO₂H and largely so by hot 2% HCl-EtOH, whereas piperonal is only slightly affected. It is concluded that lignin contains no CH₂O₂·C₆H₃ and that the CH₂O is derived from unsaturated side-chains of aromatic compounds.

XLIV. The H₂O-sol. aldehyde fraction obtained by ethanolysis of maple wood contains ~ equal amounts of syringoylacetalddehyde (I), m.p. 74—74.5°, 4:3:5:1-OH·C₆H₂(OMe)₂·CHO (II), 4:3:1-OH·C₆H₃(OMe)·CHO, and 4:3:1-OH·C₆H₂(OMe)·CO·CH₂·CHO. The structure of (I) follows from failure of the CHI₃ reaction, reduction of ammoniacal AgNO₃, formation of a disemicarbazone, m.p. 239°, and, rapidly in 3N-HCl, of a monosemicarbazone, m.p. 210—210.5°, oxidation by H₂O₂ to syringic acid (III), and cleavage by alkali to (III) and by aq. NaHSO₃ at 110° in N₂ containing O₂ to 4:3:5:1-OH·C₆H₂(OMe)₂·COMe [with, in one experiment, some (III)] [formed by oxidation to OH·C₆H₂(OMe)₂·CO·CH₂·CO₂H and subsequent fission]. Condensation of (I) with polyhydric phenols to give anthocyanidins and flavones is discussed.

R. S. C.

Tea tannin and its fermentation products.—See A., 1939, III, 951.

Conversion of *l*- into a *d*-abietic acid. T. HASSELSTROM and J. D. McPHERSON (J. Amer. Chem. Soc., 1939, 61, 2247).—When gum rosin is boiled in AcOH, saturated with HCl at 0°, and kept at room temp. for 2 weeks, the same dichlorodihydroabietic acid (I), m.p. 190.5° (decomp.; corr.), [α]_D -10° to -8.1° in EtOH, is obtained as from pure abietic acid. With boiling NaOEt-EtOH, (I) gives a *d*-abietic acid, m.p. 142—143° (corr.), [α]_D +20° in EtOH [NH(C₂H₅)₂ salt, m.p. 119—119.5° (corr.), [α]_D +3.3° in EtOH], with a small amount of (?) dihydroabietic acid.

R. S. C.

Hydroxy- and amino-derivatives of dehydroabietic acid and dehydroabietinol. L. F. FIESER and W. P. CAMPBELL (J. Amer. Chem. Soc., 1939, 61, 2528—2534).—Prep. of dehydroabietic acid is modified to give a 43% yield from crude Na abietate. Me 6-acetyldehydroabietate (I) is accompanied in the Friedel-Crafts product by a 1:1 mol. compound, m.p.

119.5—120°, of (I) and the 8-Ac ester (II), dimorphic, m.p. 137° or 153—153.5°, [α] +40°, best resolved by converting (I) into its oxime (III), m.p. 121.5—122.5°, [α] +76°. (II) gives no oxime. The structure of (II) is proved by HNO₃-oxidation to 1:2:3:4-C₆H₂(CO₂H)₄. With Ac₂O and HCl in warm AcOH, (III) gives a mixture, which by partial hydrolysis etc. yields Me 6-aminodehydroabietate (IV) (62%), m.p. 137—137.5°, [α] +81° [hydrochloride, m.p. (+H₂O) 250—260° (decomp.; sinters at ~160°) or (anhyd.) >290° (vac.)], 6-aminodehydroabietic acid (24%), m.p. 214—215° (vac.), [α] +82° (hydrochloride, m.p. >295°; Ac derivative, m.p. 255—256°, [α] +80°), and 6-carboxymethylamidodehydroabietic acid (6%), m.p. 254—255°, [α] +82°, hydrolysed by boiling KOH-Bu^oOH to 6-carboxydehydroabietic acid, +H₂O, m.p. >280°, [α] +71° in 80% EtOH. (IV) gives a Ac₂, m.p. 150—151°, [α] +75°, and Ac₁ derivative, cryst., [α] +79°. A diazo-reaction converts (IV) into Me 6-hydroxydehydroabietate (68%) (V), m.p. 157—157.5°, [α] +71°. H₂-Cu chromite reduces Me dehydroabietate in dioxan at 250°/87—71 atm. to dehydroabietinol, b.p. 177°/1 mm., [α] +53° (3:5-dinitrobenzoate, m.p. 123—124°), and (IV) to 6-aminodehydroabietinol (VI), m.p. 139.5—140°, [α] +72° (hydrochloride, cryst., [α] +63°). Ag₂O-MeI, followed by NH₄I, converts (VI) into a methiodide, m.p. 152—152.5° (decomp.), which at 140°/1—2 mm. yields 6-dimethylaminodehydroabietinol Me ether [hydrochloride, m.p. 226—227° (decomp.; vac.), [α] +78°]. 6-Hydroxydehydroabietinol, m.p. 180—181.5°, [α] +72°, is oestrogenic; it is obtained from (VI) by a diazo-reaction, but not by hydrogenation of (V). M.p. are corr. [α] are [α]_D²⁵ in EtOH, unless otherwise stated.

R. S. C.

Saponins and sapogenins. XI. Neotigogenin, a steroid sapogenin. L. H. GOODSON and C. R. NOLLER. XII. Product of direct oxidation of echinocystic acid with dichromic acid. R. N. JONES, D. TODD, and C. R. NOLLER (J. Amer. Chem. Soc., 1939, 61, 2420—2421, 2421—2423).—XI. From *Chlorogalum pomeridianum* are isolated small amounts of neotigogenin (I), +xEtOH, m.p. 202—203°, C₂₇H₄₄O₃, [α]_D²⁵ -64.9° in CHCl₃, as acetate, m.p. 174—176°, [α]_D²⁵ -73.4° in CHCl₃. CrO₃ oxidises (I) to neotigogenone, C₂₇H₄₂O₃, m.p. 211—214°, [α]_D²⁵ -60.6° in CHCl₃ [oxime, m.p. 231—232° (decomp.)]. HCl-EtOH converts tigogenin into a product, m.p. 189.5—194.5°, which probably contains no (I).

XII. Norechinocystenone and norechinocystenedione (II) (A., 1939, II, 333) show weak absorption max. at 2900—3000 (due to CO) and 2450—2500 Å. CO:C:C is thus absent. *iso*Norechinocystenedione (III) shows no CO absorption in Et₂O and only an inflexion in EtOH, although the CO max. (2930 Å.) is developed by NaOH in moist EtOH. Hot KOH-EtOH converts (III) into (II). Norechinocystenone-oxime, m.p. 253—253.5°, norechinocystenedione-oxime, m.p. 248—249°, and "isonorechinocystenedionemono-oxime," m.p. 254—257° (preheated at 240°), are prepared. A cyclic semiacetal structure is suggested for (III).

R. S. C.

Derivatives of tetrone acid. F. REUTER and R. B. WELCH (J. Proc. Roy. Soc. New South Wales,

1939, 72, 120—128).—The yield of tetrone acid (I) obtained by the reduction of α -bromotetrone acid in presence of Pd-C can be increased to 48% by addition of solid $\text{Ba}(\text{OH})_2$ to the reaction mixture. In the prep. of (I) $\text{Ba}(\text{OH})_2$ is superior to NaOH for the hydrolysis of α -carbethoxytetrone acid (II). The product obtained by heating $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (III) at $120^\circ/25$ —30 mm. is a mixture of (I) with a bromotetrone acid. In a variety of solvents (III) and NaOEt afford Et_2 2 : 5-diketocyclohexane-1 : 4-dicarboxylate. OEt-CHMe-COCl and $\text{CHNa}(\text{CO}_2\text{Et})_2$ condense to α -carbethoxy- γ -methyltetrone acid, which could not be resolved into its optical antipodes by strychnine in EtOH. (II) and $\text{NHPh}\cdot\text{NH}_2$ afford the phenylhydrazone, $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_2$, m.p. 157° (decomp.). Treatment of Et_2 acetosuccinate with Br in CHCl_3 followed by removal of solvent and HBr in a vac. and prolonged heating of the residue at 95 — $100^\circ/20$ —30 mm. gives α -carbethoxymethyltetrone acid, m.p. 93 — 94° , in considerably improved yield; it is hydrolysed to α -carboxymethyltetrone acid, m.p. 173° . Similarly Et_2 α -bromoacetylglutarate is cyclised to α - β' -carbethoxyethyltetrone acid, m.p. 78 — 79° , hydrolysed to α - β' -carboxyethyltetrone acid, m.p. 175° . Successive bromination and cyclisation of Et_2 propionylsuccinate gives non-cryst. γ -methyl- α -carbethoxymethyltetrone acid, b.p. $172^\circ/0.5$ mm. (γ -methyl- α -carboxymethyltetrone acid, m.p. 164°). Et_2 α -propionylglutarate is converted into the very hygroscopic γ -methyl- α - β' -carboxyethyltetrone acid, b.p. $190^\circ/0.45$ mm. (corresponding acid, m.p. 134°). (II) is transformed by successive treatments with Na and AcCl in dioxan into α -carbethoxy- α -acetyl tetrone acid, m.p. 95° , hydrolysed by $\text{Ba}(\text{OH})_2$ at 60° to α -acetyl tetrone acid, m.p. 79° . H. W.

2-Furfuryl bromide. J. E. ZANETTI and J. T. BASHOUR (J. Amer. Chem. Soc., 1939, 61, 2249—2251).—Evaporating the Et_2O solution at 10 mm. gives 2-furfuryl bromide, b.p. 32.5 — 34.5° , which is very unstable and explodes if the HBr formed by decomp. accumulates. R. S. C.

Hydroxymethylfurfuraldehyde derivatives of high mol. wt. T. ISEKI and T. SUGIURA (J. Biochem. Japan, 1939, 30, 113—118).—2 : 2'-Di(furylmethyl) ether 5 : 5'-dialdehyde is reduced by Ag_2O -aq. NH_3 to 5 : 5'-dicarboxy-2 : 2'-di(furylmethyl) ether, m.p. 209 — 210° (cf. A., 1933, 719) [M_{e_1} , m.p. 144 — 146° , M_{e_2} , m.p. 154° , and Et_2 ester, m.p. 71° ; chloride (I), m.p. 98 — 99° ; $\text{CH}_2\text{Cl}\cdot\text{CH}_2$ ester, m.p. 78 — 79°]. (I) with $\text{C}_5\text{H}_5\text{N}$ condenses to tetra-(2 : 2'-dimethyl-5 : 5'-furoic anhydride) ether, $\text{C}_{48}\text{H}_{32}\text{O}_{24}$, m.p. 165 — 167° . F. O. H.

Sugar-amino-acid compounds. T. ISEKI and T. SUGIURA (J. Biochem. Japan, 1939, 30, 119—123; cf. A., 1933, 719).—5 : 5'-Dicarboxy-2 : 2'-di(furylmethyl) ether chloride with NH_3 or the appropriate amine gives the corresponding carbamyl, m.p. 204° , carbamyl, m.p. 169° , carbo-o-hydroxyanil, m.p. 329° (230° ?), and carboxymethylcarbamyl derivative, m.p. 223° (Et ester, m.p. 107°). 2 : 2'-Di(furylmethyl) ether 5 : 5'-dialdehyde with 2-furoic acid and NH_2Ph in EtOH at the b.p. gives 2 : 2'-di(furylmethyl) ether 5 : 5'-di-(2-cinchonic acid), m.p. 251° . F. O. H.

Derivatives of coumaran. IV. Structure of tectorigenin. R. L. SHRINER, E. J. MATSON, and R. E. DAMSHRODER. **V. Synthesis of 4-hydroxycoumaran-3-one.** R. L. SHRINER and M. WITTE (J. Amer. Chem. Soc., 1939, 61, 2322—2327, 2328—2329; cf. A., 1938, II, 333).—IV. The isoflavone structure of tectorigenin (isolation described), m.p. 230° (Me_2 ether, m.p. 188° ; Me_3 ether unobtainable), is confirmed by synthesis of isomeric coumaranone derivatives. Iretol, $\text{CH}_2\text{Cl}\cdot\text{CN}$, and dry $\text{HCl}\cdot\text{Et}_2\text{O}$ give α -chloro-2 : 4 : 6-trihydroxy-3-methoxyacetophenone-imine hydrochloride, decomp. 164 — 165° . With hot H_2O this undergoes hydrolysis and ring-closure, yielding 3 : 5-dihydroxy-4- (I), m.p. 208.5 — 209.5° , and 6-methoxycoumaran-2-one (II), m.p. 177 — 178° . With CH_2N_2 , (I) gives 3 : 4 : 5-trimethoxycoumar-2-one (III), m.p. 142.5 — 143.5° , and with $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in abs. EtOH at 65 — 70° gives the very unstable 1- p -hydroxybenzylidene derivative, decomp. 291° (block), reduced (H_2 -PtO₂; EtOH; 3 atm.) to the impure, unstable 1- p -hydroxybenzyl derivative, m.p. 114 — 117° (decomp.). (III) yields the 1- p -anisylidene, m.p. 148 — 149° , and thence the 1- p -anisyl derivative, m.p. 93 — 94° . Similarly are obtained from (II) 3 : 5 : 6-trimethoxy- (IV), m.p. 153.5 — 154.5° , 3 : 5-dihydroxy-6-methoxy-1- p -hydroxybenzylidene-, decomp. 282° (block), unstable, and 1- p -anisyl-, m.p. (impure) ~ 155 — 170° (decomp.), and 3 : 5 : 6-trimethoxy-1- p -anisylidene-, m.p. 195 — 196° , and 1- p -anisyl-, m.p. 116° , -coumaran-2-one. Antiarol (modified prep.), $\text{CH}_2\text{Cl}\cdot\text{CN}$, ZnCl_2 , and HCl in Et_2O give an imine, hydrolysed to α -chloro-6-hydroxy-2 : 3 : 4-trimethoxyacetophenone, m.p. 107 — 107.5° , which with NaOAc-EtOH yields (III). 2 : 5 : 1 : 4-(OMe)₂C₆H₂(OH)₂, $\text{CH}_2\text{Cl}\cdot\text{CN}$, and HCl in Et_2O give α -chloro-2 : 4 : 6-dihydroxy-3 : 6-dimethoxyacetophenone, m.p. 150.5 — 151.5° , converted by NaOAc-EtOH into 5-hydroxy-3 : 6-dimethoxycoumaran-2-one, m.p. 180 — 181° (decomp.), and thence by CH_2N_2 into (IV).

V. 2 : 6 : 1-C₆H₃(OH)₂·COMe and boiling Ac_2O give 2 : 6-diacetoxyacetophenone, m.p. 60° , which with Br in CS_2 gives the α -Br- (I), m.p. 112° , and in AcOH the α -Br₂ derivative, m.p. 113° . 40% HBr (20 c.c.) and a trace of $\text{Na}_2\text{S}_2\text{O}_4$ in boiling 60% EtOH (80 c.c.) give α -bromo-2 : 6-dihydroxyacetophenone, m.p. 143° , converted by NaOAc and a trace of $\text{Na}_2\text{S}_2\text{O}_4$ in aq. EtOH into 3-hydroxycoumaran-2-one, m.p. 120° (sublimes from 85°) (converted by $\text{BzCl}\cdot\text{Na}_2\text{CO}_3$ -aq. COMe₂ into 2 : 3-dibenzoyloxybenzofuran, m.p. 183°), the volatility and unusual solubility of which indicate chelation of the OH and CO. M.p. are corr.

R. S. C.

Vitamin-E. XVII. Oxidation products of α -tocopherol and of related 6-hydroxychromans. L. I. SMITH, W. B. IRWIN, and H. E. UNGNADE (J. Amer. Chem. Soc., 1939, 61, 2424—2429).—The red compound (I), m.p. 109 — 110° , obtained from 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethylchroman by AgNO_3 -EtOH- HNO_3 , is 2 : 2 : 7 : 8-tetramethylchroman-5 : 6-quinone; the gummy product from dl- α -tocopherol (oily, fluorescent phenazine derivative) is also a 5 : 6-quinone. The phenazine, m.p. 151 — 151.5° , and tetramethylphenazine derivative (impure), m.p. 204 — 205° , of (I) fluoresce, particularly in ultraviolet light. H_2 -PtO₂ reduces the former to a colour-

less substance, oxidised by air. NaHSO_3 reduces (I) to a colourless substance, very rapidly oxidised in air. 2 : 3 : 1 : 4- $\text{C}_6\text{H}_2\text{Me}_2(\text{OH})_2$, isoprene, and ZnCl_2 give 6-hydroxy-2 : 2' : 7' : 8-tetramethyl-5- γ -methyl- Δ^{β} -n-butenylchroman and 2 : 2' : 2' : 7' : 8-hexamethyl-3' : 4'-dihydropyrano-5' : 6' : 5 : 6-chroman, oils, which with AgNO_3 - EtOH - HNO_3 give (I). Structures are supported by absorption spectra. Formation of the red compounds occurs only in alcohols ($\text{MeOH} > \text{EtOH} > \text{Pr}^{\beta}\text{OH} > \text{Bu}^{\gamma}\text{OH} > \text{mesitol}$), and the simultaneous production of aldehydes may be significant.

R. S. C.

7-Hydroxy-3-benzoylflavone. S. RANGASWAMI and T. R. SESHADRI (Proc. Indian Acad. Sci., 1939, 10, A, 6-8).—Resacetophenone, Bz_2O , and NaOBz at 180–190° give a mixture, converted by short treatment with 10% KOH - EtOH into 7-hydroxy- and 7-hydroxy-3-benzoyl-flavone, m.p. 264–265°. The latter product is hydrolysed by boiling 5% Na_2CO_3 to 7-hydroxyflavone and BzOH . The method of Robinson *et al.* (A., 1926, 1149) usually gives large amounts of 3-Bz compound, which can often be separated from the 7-OBz-compound by utilising the varying rates of hydrolysis of C- and O-Bz.

R. S. C.

Phenolphomphthalein. B. Hoř (Compt. rend., 1939, 209, 321–324).—Equimol. amounts of homophthalic anhydride (I) with PhOH and SnCl_4 at 125° afford 3-p-hydroxyphenylisocoumarin (II), m.p. 227° (acetate, m.p. 161°), also obtained by cyclisation of 4'-hydroxydeoxybenzoic-2-carboxylic acid (III) (cf. A., 1939, II, 429). Phenolphomphthalein, m.p. 160–170°, is also formed, has properties like those of phenolphthalein, and exists in three tautomeric forms. In NaOH (II) gives an intense yellow solution which fades when the Na salt of (III) is formed. (III), also formed from (I) and PhOH in presence of conc. H_2SO_4 , melts at about 211°, being converted into (II). (II) or (III) with N_2H_4 and NH_2OH affords a homophthalazone, m.p. 243° (decomp.), and a lactazone, m.p. 258°, respectively.

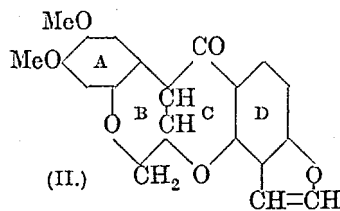
J. L. D.

Yellow pigment of Papaver nudicaule. I. J. R. PRICE, (Sir) R. ROBINSON, and (in part) R. SCOTT-MONCRIEFF (J.C.S., 1939, 1465–1468).—Nudicaulin chloride (I) has been isolated as a yellow amorphous powder; a formula of the order $\text{C}_{30}\text{H}_{38}\text{O}_{15}\text{NCl}$ containing 0.3 OMe is indicated. Hydrolysis affords glucose in amount > the theoretical for a monoglucoside but considerably < that required for a diglucoside; this is possibly due to condensation of the aglycone with glucose. The presence of $p\text{-OH-C}_6\text{H}_4$ and of NH_2 is indicated. After methylation and oxidation (KMnO_4), anisic acid is obtained. The formation of a ψ -base is the chief reason for suspecting the presence of a flavylum salt structure, but this is not decisive.

F. R. S.

Active principles of leguminous fish-poison plants. III. Structure of elliptone. S. H. HARPER (J.C.S., 1939, 1424–1427).—During the prep. of dehydroelliptone (I) from *l*-elliptone (II), *O*-acetylleptilolone, m.p. 175.5°, hydrolysed to elliptolone, m.p. 228°, is obtained. Zn and KOH with (I) give elliptic acid, m.p. 190° (*Me* ester, m.p. 143°), which is

oxidised (H_2O_2) to derric acid. It follows that the degradation has taken the same course as with rotenone and isorotenone, and therefore rings A, B, and C of these are identical with those in (II). Degradation of (I) with KOH - EtOH affords 4-hydroxycoumarone-5-carboxylic acid, m.p. 221° (*Me*



ester, m.p. 105°), also obtained by carboxylation of 4-hydroxycoumarone. This confirms the structure assigned to (II). The isomerism of the α - and β -oximes of rotenone is due to dimorphism. F. R. S.

Absorption spectra of some sulphur compounds.—See A., 1939, I, 507.

Oxidation products of pyrrole amines. III. T. AJELLO (Gazzetta, 1939, 69, 453–459).—Zn, Fe, or Cu and AcOH , etc., which with oximinophenylmethylpyrrole (I) give amorphous products, reduce 3-oximino-2 : 5-diphenylpyrrole (II) to aminodiphenylpyrrole (III). Cu powder in AcOH at room temp., however, reduces (II) slowly to azoxydiphenylpyrrole (IV), m.p. 170–172° [*picrate*, m.p. 180° (decomp.)], also obtained by oxidation of (III) by H_2O_2 - AcOH , by CrO_3 - AcOH , or by FeCl_3 . (IV) is readily reduced to (III). FeSO_4 or CuCl and (I) yield benzoylmethylisooxazole.

E. W. W.

Oximinopyrroles. XII. Transformation of the pyrrole into the pyrimidine nucleus. T. AJELLO (Gazzetta, 1939, 69, 460–470).—4-Oximino-2 : 3 : 5-triphenylpyrrole (I) when steam-distilled gives HCN , PhCHO , NH_3 , and an amorphous product. With HCl in CHCl_3 , (I) and 3-oximino-2 : 5-diphenylpyrrole (II) give only their hydrochlorides. With PCl_5 in CHCl_3 , (I) gives 4-hydroxy-2 : 3 : 6-triphenylpyrimidine (III), and a substance, m.p. 228°, converted by boiling AcOH into (III). Similarly (II) gives 4-hydroxy-2 : 6-diphenylpyrimidine.

E. W. W.

Mixed platinum hydroxylamine tetrammines.—See A., 1939, I, 533.

2'-Aminopyridide of *p*-nitrobenzenesulphinic acid.—See B., 1939, 1077.

Indoles. VII. Derivatives of 7-nitroindole. G. K. HUGHES, F. LIONS, and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1939, 72, 209–220).—*o*-Nitrophenylhydrazones of α -CO esters are obtained by adding KOH to a well-stirred solution of the ester in EtOH at 0° followed immediately by the diazo-solution from $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$. The following methods of cyclisation are used : (I) the *o*-nitrophenylhydrazone (I) is boiled with glacial AcOH for several hr.; (I) is kept in conc. H_2SO_4 (2) or HCl - EtOH (3); (I) is heated under reflux with (1 : 10) H_2SO_4 (4) or conc. HCl (5); (I) is heated with ZnCl_2 in *cumene* (6) or EtOH (7); (I) is boiled with a solution of HBr in AcOH (8). The following transitions are described, the figures in parentheses indicating the methods of cyclisation used : *Et pyruvate o-nitrophenylhydrazone*, m.p. 106° (by 5 but not by 1, 2, or 3), to 7-nitroindole-2-carboxylic acid, m.p. 231°, which is not reduced by $\text{FeSO}_4\text{-NH}_3$ to the NH_2 -compound but is decarb-

oxylated in glycerol at 220° to 7-nitroindole, m.p. 113°; *Et* α -ketobutyrate *o*-nitrophenylhydrazine, m.p. 94°, by (1) and (3) to a yellow isomeride, m.p. 68°, and by (2) to *Et* 7-nitro-3-methylindole-2-carboxylate, m.p. 115° (acid, m.p. >270°); non-cryst. *Et* α -ketovalerate *o*-nitrophenylhydrazine, by (2) or (6) but not by (1) to *Et* 7-nitro-3-ethylindole-2-carboxylate, m.p. 85° [acid, m.p. 245° (decomp.)]; non-cryst. *Et* α -ketohexanoate *o*-nitrophenylhydrazine by (2) or (6) but not by (1) to *Et* 7-nitro-3-propylindole-2-carboxylate, m.p. 70° (acid, m.p. 196°); *Et* phenylpyruvate *o*-nitrophenylhydrazine, m.p. 68°, by (3) or (8) but not by (1), (2), (4), (5), or (6) to *Et* 7-nitro-3-phenylindole-2-carboxylate, m.p. 112°; *Et* *H* ketopimelate *o*-nitrophenylhydrazine, m.p. 122°, by (5) but not by (2) or (6) to γ -7-nitro-2-carboxyindolylbutyric acid, m.p. 171°, and by (7) to 7-nitro- γ -2-carbethoxyindolylbutyric acid, m.p. 184°. Acetone-*o*-nitrophenylhydrazine, m.p. 70°, could not be cyclised by (5) or (6); *Et*₂ ketone *o*-nitrophenylhydrazine, m.p. 60°, by (5) but not by (1) to 7-nitro-3-methyl-2-ethylindole, m.p. 104°; isobutaldehyde-*o*-nitrophenylhydrazine, m.p. 59°, by (5) to (?) 2 : 2'-isobutylidenedi-(7-nitro-3 : 3'-dimethylindolenine), m.p. 154°; cyclopentanone-*o*-nitrophenylhydrazine, m.p. 64°, not converted into an indole by (2), (4), or (5); acetophenone-*o*-nitrophenylhydrazine, m.p. 138°, not cyclised by (2), (5), or (6); propiophenone-*o*-nitrophenylhydrazine, m.p. 120°, not cyclised by (5) but giving by (6) a mixture of red and orange crystals, m.p. ~70°; deoxybenzoin-*o*-nitrophenylhydrazine, m.p. 125°, not cyclised by (5) or (6); 3-acetylpyridine-*o*-nitrophenylhydrazine, m.p. 144°, not cyclised by (5) or (6). H. W.

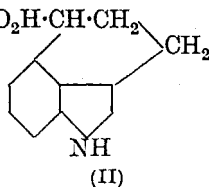
Indoles. VIII. 3-Hydroxymethylindole-2-carboxylactone. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 72, 221—227).—Addition of PhN₂Cl to acetobutyrolactone in 2.5% NaOH gives α -ketobutyrolactonephenylhydrazine (I), m.p. 220°, which could not be converted into an indole by saturated HCl-EtOH, EtOH-H₂SO₄, conc. HCl, conc. H₂SO₄, glacial AcOH, or HBr in AcOH. Gradual addition of conc. HCl to a solution of (I) in hot AcOH followed by short boiling gives a small yield of 3-hydroxymethylindole-2-carboxylactone (II), m.p. 209°, which is insol. in boiling Na₂CO₃ or cold NaOH but is sol. in boiling NaOH. 3-Hydroxymethylindole-2-carboxylic acid has m.p. 244—245° (decomp.). (II) is transformed by N₂H₄·H₂O in boiling H₂O into the hydrazide of 3-hydroxymethylindole-2-carboxylic acid, m.p. 195—200° (vigorous gas evolution) when rapidly heated, which passes when heated at 180—200° into the compound, C₁₀H₉ON₂, m.p. 285°, and affords a :CHPh derivative, m.p. 235°. 3-Hydroxymethylindole-2-carboxylic acid phenylhydrazide has m.p. 196°. (I) could not be caused to react satisfactorily with KCN. H. W.

Identification reactions on isaceen [diacetyldihydroxyphenylisatin]. M. J. SCHULTE (Pharm. Weekblad, 1939, 76, 1256—1257).—Diacetyldihydroxyphenylisatin (I) (10 mg.) is boiled with EtOH (1 c.c.) and 0.1N-NaOH (1 c.c.); a violet colour develops, which becomes deep blue on cooling and adding 0.5N-Br (1 drop). The blue colour is extracted with CHCl₃. An orange-red colour is produced with

Ehrlich's diazo-reagent, NaOH, and NaNO₂; when the solution is acidified (H₂SO₄) and boiled the colour changes to yellow and EtOAc is formed. (I) gives a purple colour in H₂SO₄. S. C.

Preparation of trimethyleneindole derivatives.

R. G. GOULD, jun., and W. A. JACOBS (J. Biol. Chem., 1939, 130, 407—414).—3-Amino-1-naphthoic acid nitrate, m.p. 225—230° (decomp.), and conc. H₂SO₄ at -30° to -40° give (?) 5- (I), m.p. 303—308° (decomp.), and 8-nitro-3-amino-1-naphthoic acid, m.p. 230—231° (decomp.) [Ac derivative, m.p. 274—276° (decomp.)]. Fe(OH)₂ reduces (I) to 3 : (?) 5-diamino-1-naphthoic acid, unstable [Ac₂ derivative, m.p. 323—330° (decomp.)], but (II) thus yields 3-amino-naphthostyryl, m.p. 238—240° [picrate, m.p. 245—250° (decomp.)]; Ac derivative, m.p. 300—302° (decomp.); obtained also with difficulty from 3 : 8 : 1-(NH₂)₂C₁₀H₅·CO₂H], reduced by Na-BuOH to (*inter alia*) 3 : 4- β -aminotrimethyleneindole, a gum [picrate, m.p. 242—248° (decomp.)]; hydrochloride, m.p. 215—222° (decomp.), hygroscopic]. 1 : 4-C₁₀H₆(CO₂H)₂ and HNO₃ (*d* 1.58) at 0° give the 5-NO₂-derivative, m.p. (crude) 270—274° (decomp.), reduced by Fe(OH)₂ to naphthostyryl-4-carboxylic acid (I), m.p. >350°, the NH₂ salt of which with Na-BuOH yields 3 : 4- γ -carboxytrimethyleneindole (II), m.p. 142—144° [Me ester, m.p. 82—84°; picrate, m.p. 168—170° (decomp.)]. Na-BuOH reduces the Me, m.p. 260—261°, or Et ester (III), m.p. 217—218°, of (I) to 3 : 4- γ -hydroxytrimethyleneindole, m.p. 147—150° (decomp.). Catalytic hydrogenation of (III) yields the lactam, m.p. 175—177°, of 8-amino-4-carbethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene-1-carboxylic acid, which with boiling NaOH affords 8-amino-1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 4-dicarboxylic acid [hydrochloride, m.p. 300—309° (decomp.)]. R. S. C.



Synthesis of peptide-like derivatives of amino-hydrocarbostyryl. Amyostatic poisons. T. SASAKI and T. HASHIMOTO (Proc. Imp. Acad. Tokyo, 1939, 15, 233—238).—Gradual alternate addition of NaHCO₃ and CHMeBr·COBr to dl-3-aminohydrocarbostyryl hydrochloride (I) and NaHCO₃ at 0° yields dl-3- α -bromopropionamido-dl-hydrocarbostyryl (II), m.p. 228—229° (decomp.), transformed by NH₃-EtOH at 100° into dl-3-(dl- α -alanylamido)hydrocarbostyryl (III), C₉H₉ON₂·CO·CHMe·NH₂, m.p. 180—182° [hydrochloride, m.p. 245—246° (decomp.)]. Treatment of (II) with the requisite amine leads to dl-3-(dl-N-methyl- α -alanylamido)-, m.p. 187—188° [hydrochloride, m.p. 261—262° (decomp.)], -(dl-N-dimethyl- α -alanylamido)-, m.p. 163—164° [hydrochloride, m.p. 248—249° (decomp.)], -(dl-N-ethyl-2-alanylamido)- [hydrochloride, m.p. 270—271° (decomp.)], and -(dl-N-diethyl- α -alanylamido)-, m.p. 140—141° [hydrochloride, m.p. 385—386° (decomp.)], -hydrocarbostyryl. CH₂Cl·CH₂·COCl and (I) afford dl-3-(β -chloropropionamido)hydrocarbostyryl, m.p. 226—227° (decomp.), converted into dl-3-(β -alanylamido)hydrocarbostyryl (IV), m.p. 227—228° (decomp.) [hydrochloride, m.p. 265—266° (decomp.)], which affords N-Me₁ [hydrochloride (+2H₂O)], N-Me₂, m.p. 176—177° [hydrochloride, m.p. 305—306°

(decomp.), N-Et₁, m.p. 177—178° [hydrochloride, m.p. 236—237° (decomp.)], and N-Et₂, m.p. 156—157° [hydrochloride, m.p. 308—309° (decomp.)], derivatives. CH₃EtBr·COBr and (I) yield dl-3-(dl-α-bromobutyramido)hydrocarbostyryl, m.p. 220—221° (decomp.), whence dl-3-(dl-α-aminobutyramido)hydrocarbostyryl (V), m.p. 169—170° (hydrochloride) (+1H₂O). dl-3-(dl-α-Bromoisovaleramido)-, m.p. 239—240° (decomp.), is transformed into dl-3-(dl-α-aminoisovaleramido)hydrocarbostyryl (VI), m.p. 269—270° [hydrochloride, m.p. 295—296° (decomp.)]. Similarly, dl-3-(dl-α-bromohexamido)-, m.p. 190—192°, affords dl-3-(dl-leucylamido)hydrocarbostyryl (VII), m.p. 255—257° [hydrochloride, m.p. 304—305° (decomp.)]. The amyostatic activity of the bases decreases in the sequence (III), (IV), (V), (VI), (VII) parallel with their solubility in acid. H. W.

Synthesis of diaminohydrocarbostyryl by the diketopiperazine method. Amyostatic poisons. IV. T. SASAKI and H. UEDA (Proc. Imp. Acad. Tokyo, 1939, 15, 239—242).—Diacetylglycine anhydride (I), 2:4-(NO₂)₂C₆H₃·CHO, anhyd. NaOAc, and C₅H₅N in PhMe at 130—135° give di-2:4-dinitrobenzylidenediketopiperazine, converted by red P and boiling HI (d 1.7) into 3:7-diaminohydrocarbostyryl, m.p. 207° [dihydrochloride; Bz₂, m.p. 285—286°, and Ac₂, m.p. 293° (decomp.)], derivatives]. Similarly, (I), 2:6-(NO₂)₂C₆H₃·CHO, and NH₄Et₂ in PhMe at 130—140° afford di-2:6-dinitrobenzylidenediketopiperazine, converted into 3:5-diaminohydrocarbostyryl (dihydrochloride; Ac₂ derivative, decomp. ~325°). The amyostatic action of 3-aminohydrocarbostyryl is nullified by the introduction of NH₂ at C₍₅₎ or C₍₇₎. H. W.

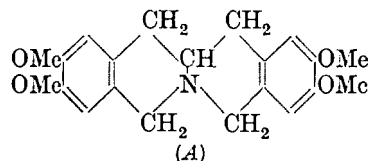
Co-ordination compounds with 8-aminoquinoline as a chelate group. G. J. BURROWS and E. RITCHIE (J. Proc. Roy. Soc. New South Wales, 1939, 72, 113—117).—If the four valencies of a quadri-covalent metal are planar, *cis*- and *trans*-forms of their compounds with 8-aminoquinoline (I) should exist but if the valencies are tetrahedrally disposed optically active forms should be obtainable. In all cases investigated the complex compound appears to be homogeneous and no sign of *cis-trans* isomerism has been detected. The following compounds are obtained by mixing conc. solutions of the metallic salt in H₂O and of (I) in EtOH; after 30 min. the ppt. is collected and dried in air: [Cu(C₉H₈N₂)₂]SO₄·7H₂O; [Cu(C₉H₈N₂)₂]SO₄·5H₂O; [Cu(C₉H₈N₂)₂]Cl₂·5H₂O; [Cu(C₉H₈N₂)₂]Cl₂·H₂O; [Cu(C₉H₈N₂)₂](NO₃)₂·6H₂O; [Fe(C₉H₈N₂)₂]SO₄·6H₂O; [Ni(C₉H₈N₂)₂]Cl₂·2H₂O; [Ni(C₉H₈N₂)₂]Cl₂·16H₂O; [Ni(C₉H₈N₂)₂](NO₃)₂·4H₂O; [Ni(C₉H₈N₂)₂](NO₃)₂·10H₂O; [Co(C₉H₈N₂)₂]Cl₂·H₂O. H. W.

Identification of 4-nitroacridone-1-carboxylic acid [by conversion into] 4-aminoacridine. K. MATSUMURA (J. Amer. Chem. Soc., 1939, 61, 2247—2248).—The identity of 4-nitroacridone-1-carboxylic acid (A., 1938, II, 246) is confirmed by conversion of the derived aminoacridone by Na-Hg in 33% aq. EtOH into 4-aminoacridine, new m.p. 178° (uncorr.), 182.3° (corr.) [hydrochloride, new m.p. 285° (decomp.)] (cf. Lehmsstedt, *ibid.*, 419). New m.p. 218° (uncorr.)

[223.5° (corr.)] and 328—329° (decomp.) are recorded for 2-aminoacridine and its hydrochloride.

R. S. C.

Synthesis of dibenzopyridocoline derivatives. III. **Synthesis of 3':4':3'':4''-tetramethoxy-1:4:5:8-tetrahydro-(1':6':2:3:1'':6'':6:7-dibenzopyridocoline).** S. SUGASAWA, K. KAKEMI, and H. KAZUMI (Proc. Imp. Acad. Tokyo, 1939, 15, 223—225; cf. A., 1938, II, 378; 1939, II, 343).—Dihomoveratryl ketone, m.p. 99—101° (oxime, m.p. 108—111°), is not obtained by the thermal decomp. of the alkaline-earth homoveratrates but is prepared in 45—50% yield from the Pb salt. It is transformed by Leuckart's method into formdihomoveratryl-methylamide, m.p. 129—130°, which is converted by POCl₃ in dry xylene into the non-cryst. 6:7-dimethoxy-3-3':4'-dimethoxybenzyl-3:4-dihydroisoquinoline (I) (perchlorate, m.p. 230—232°). The hydrochloride of the base is reduced catalytically to 6:7-dimethoxy-3-3':4'-dimethoxybenzyl-1:2:3:4-tetrahydroisoquinoline (hydrochloride, m.p. 206°). (I) is readily converted by HCl and CH₂O at 100° into 3':4':3'':4''-tetramethoxy-1:4:5:8-tetrahydro-(1':6':2:3:1'':6'':6:7-dibenzopyridocoline (A) [hydrochloride (+0.5H₂O), decomp. 271—272°].



H. W.

Synthesis of coloured derivatives of nirvanol.

II. **N-Benzylazo-compounds.** S. P. LINGO [with H. R. HENZE] (J. Amer. Chem. Soc., 1939, 61, 2029—2032; cf. A., 1939, II, 344).—5-Phenyl-5-ethylhydantoin, *p*-NO₂·C₆H₄·CH₂Cl, and NaOMe in hot MeOH give 5-phenyl-3-*p*-nitrobenzyl-5-ethylhydantoin, m.p. 177—177.5°, reduced by H₂-Raney Ni at 100°/20 atm. to the 3-*p*-NH₂·C₆H₄·CH₂ derivative (I), m.p. 171.7°. NaNO₂-HCl, followed by CO(NH₂)₂, gives the diazonium salt, which by coupling yields 5-phenyl-3-β-dimethylaniline-, m.p. 228.5—229°, -3-β-naphthylamine- (II) m.p. (crude) ~120° (decomp. from 100°) [reduced by Zn-HCl-AcOH to (I); pyrolysis and subsequent reduction give (I) and 1:2-C₁₀H₆(NH₂)₂], -3-phenol-, m.p. 245—247° (later decomp.), -3-α-, m.p. ~120—148°, decomp. ~150°, and -3-β-naphthol- (III), m.p. 212—213°, -3-1':5'-dihydroxynaphthalene-, decomp. 196° (sinters at 194°), and -3-4'-hydroxy-3'-carboxybenzene-, darkens at ~125°, m.p. 133—134°, -azobenzyl-5-ethylhydantoin; these products, except (II) and (III) which are too insol., dye wool and silk. M.p. are corr.

R. S. C.

Colour in relation to chemical constitution of organic and inorganic salts of oximino-pyrazolones and -isooxazolones. S. DUTT and (Miss) I. N. D. DASS (Proc. Indian Acad. Sci., 1939, 10, A, 55—64).—CH₂Bz·CO₂Et and NH₂OH·HCl in boiling AcOH give 3-phenylisooxazolone, m.p. 174° [N·OH derivative (I), m.p. 130° (lit., 120°)]. OH·N·C·Ac·CO₂Et (improved prep.) and NH₂OH·HCl in AcOH at 100° give 4-oximino-3-methylisooxazolone (II), m.p. 150°. Prep. of 3-phenyl-, m.p. 235°

[N·OH derivative (III), m.p. 188°], and 4-oximino-3-methylpyrazolone (IV), m.p. 217° (lit., 130°), is modified. Salts of (I) and (II) are purple or deep magenta in solution (absorption max. at ~5800 Å.), existing as $\text{CR}\cdot\text{C}(\text{NO})\text{N} \rightarrow \text{C}\cdot\text{OH}$, which contains the highly strained NO (cf. A., 1938, II, 507). However, the corresponding salts of (III) and (IV) exist as $\text{CR}\cdot\text{C}(\text{N}\cdot\text{OH})\text{N} \rightarrow \text{C}\cdot\text{OH}$, do not contain NO, and are thus only orange (absorption max. at ~4800 Å.). The salts dissociate in H₂O and develop their full colour in, e.g., COMe₂ only if a little H₂O is present. The following salts of (I), (II), (III), and (IV), respectively, are described: NH₂Me, m.p. 122°, 107°, 155°, 167°; NH₂Et, m.p. 112°, 108°, 170°, 135°; NHMe₂, m.p. 102°, 102°, 185°, 161°; NHEt₂, m.p. 103°, 87°, 193°, 173°; NMe₃, m.p. 110°, 72°, 185°, 169°; NH₂Bu^a, m.p. 82°, 112°, 176°, 134°; piperidine, m.p. 121°, —, 211°, 158°; Na, m.p. 110°, 210°, —; K, m.p. 122°, —, 239°, 273°; NH₄, m.p. 86°, 96°, 184°, 214° (all m.p. with decomp.). R. S. C.

5-Sulphonylbarbituric acids. E. L. D'OUVILLE, F. J. MYERS, and R. CONNOR (J. Amer. Chem. Soc., 1939, 61, 2033—2036).—5-*p*-Toluenesulphonyl-5-ethylbarbituric (I) and -thiobarbituric acid (II) are rather unstable. 5:5-Disulphonylbarbituric acids could not be obtained, probably because of their instability. (I) has no hypnotic action. Alloxan hydrate (III) and CH₂Ph·SH in dry dioxan-HCl at <0° or AcOH-Ac₂O at 0° give 5-hydroxy-, m.p. 169—174° (decomp.) [with (CH₂Ph·S)₂, formed by reduction of (III)], and 5-acetoxy-5-benzylthiobarbituric acid, m.p. 210—235° (decomp.; pink at 190°), respectively. *p*-C₆H₄Me·SH does not condense with (III). 5:5-Dibromobarbituric acid and *p*-C₆H₄Me·SO₂Na·2H₂O (IV) in abs. MeOH at room temp. give 40% of Na 5-bromobarbiturate and *p*-C₆H₄Me·SO₂Br, the latter product reacting with more (IV) to give (*p*-C₆H₄Me·SO₂)₂ (V). 5-Bromo-5-ethylbarbituric acid and (IV) in abs. MeOH at room temp. give 20% (8% at 64°) of (I), m.p. 200.5—203.5° (decomp.), *p*-C₆H₄Me·SO₂·CHET·CO·NH₂ [due to fission of (I)], and 18% of (V). 5-Bromo-5-ethylthiobarbituric acid similarly (at 5°) gives 20% of (II), m.p. 179.9—180°, unstable when kept. R. S. C.

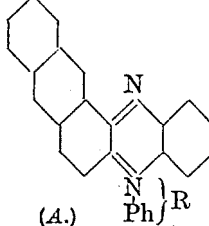
Desmotropism of xanthine derivatives. T. B. JOHNSON and J. C. AMBELANG (J. Amer. Chem. Soc., 1939, 61, 2483—2485).—No purine could be obtained from alloxan by CH₂(NH₂)₂ or (CH₂·NH₂)₂ or from alloxan-4-imine-5-oxime by *o*-C₆H₄(NH₂)₂. (CH₂·NH₂)₂ in HCl-H₂O or -EtOH gives the "anil-hydrate," $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{C}(\text{OH})\cdot\text{NH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, m.p. ~214° (decomp.) [hydrochloride, +H₂O, m.p. 225—230° (decomp.)]. R. S. C.

Quinazolines. VIII. Methyl esters of 1:3-dimethylbenzoylenecarbamide-5-carboxylic acid and 2:4-dimethoxyquinazoline-5-carboxylic acid. N. A. LANGE, D. C. CHISHOLM, and J. L. SZABO (J. Amer. Chem. Soc., 1939, 61, 2170—2171; cf. A., 1935, 99).—Contrary to Scott *et al.* (J.C.S., 1921, 119, 664), 2:4-diketo-1:2:3:4-tetrahydroquinazoline-5-carboxylic acid (I), new m.p. 346°

(block), with Me₂SO₄-alkali gives the 1:3-Me₂ derivative, m.p. 318°. The Me ester (II), new m.p. 307—309°, of (I) is obtained by HCl-MeOH or, best, by SOCl₂ [gives the chloride, m.p. 331—332° (decomp.)], followed by MeOH, and with Me₂SO₄-KOH-H₂O gives Me 2:4-diketo-1:3-dimethyl-1:2:3:4-tetrahydroquinazoline-5-carboxylate, new m.p. 144.4—145.5° (corr.), obtained less well by the method of Scott *et al.*, who misinterpreted its nature. With PCl₅-POCl₃, followed by NaOMe-MeOH, (I) gives Me 2:4-dimethoxyquinazoline-5-carboxylate, m.p. 134.5—135.5° (corr.), hydrolysed by boiling, dil. HCl to (II). The Et, m.p. 297—299°, and CH₂Ph ester, m.p. 257—261°, and amide, m.p. 359°, of (I) are described.

R. S. C.

Flavinduline derivatives. X. K. YAMADA and I. IKOMA (J. Soc. Chem. Ind. Japan, 1939, 42, 228—229B; cf. A., 1938, II, 380).—



The solubility, colour reactions, dyeing properties, and fastness of the dyes (A, R = Cl + 0.5ZnCl₂, m.p. 240—242°; R = Br, m.p. 213—215°; R = I, m.p. 143—145°) derived from anthra-1:2-quinone and *o*-NH₂·C₆H₄·NHPh, are described. H. W.

Synthesis of 1-6'-amino-2'-methyl-5'-pyrimidylmethyl-2-methyl-3-β-hydroxyethylpyridinium bromide hydrobromide. F. C. SCHMELKES and R. R. JOINER (J. Amer. Chem. Soc., 1939, 61, 2562—2563).—Synthesis of the following is reported without details by the methods indicated in parentheses: 3-nitro-6-hydroxy- (from 3-nitro-6-amino-2-methylpyridine), 6-chloro-3-nitro- (by PCl₅), 3-amino- (by H₂-Pd), m.p. 113°, 3-cyano- (Sandmeyer), m.p. 58°, and 2-acetyl-, b.p. 75—78°/2 mm., -2-methylpyridine; 2-methyl-3-β-hydroxyethylpyridine (successive reactions with Br, KOAc-EtOH, and then reduction), b.p. 125°/3 mm. (picrate, m.p. 125°; acetate, b.p. 90—92°/3 mm.). With 6-amino-2-methyl-5-bromomethylpyrimidine hydrobromide this gives 1-6'-amino-2'-methyl-5'-pyrimidylmethyl-2-methyl-3-β-hydroxyethylpyridinium bromide hydrobromide, m.p. 247°. 2-Methyl-5-β-hydroxyethylpyridine, b.p. 103°/2 mm., and 1-6'-amino-2'-methyl-5'-pyrimidylmethyl-2-methyl-5-β-hydroxyethylpyridinium bromide hydrobromide, m.p. (?) 245°, are also reported. R. S. C.

Bilichrysins. New type of bile pigment. R. LEMBERG and W. H. LOCKWOOD (J. Proc. Roy. Soc. New South Wales, 1939, 72, 69—74).—Gradual addition of 0·IN-I (≡2 atoms) in EtOH to mesobiliverdin and Zn(OAc)₂ in MeOH containing NH₃ gives mesobiliviolin II, which passes when kept in CHCl₃ into mesobiliviolin III (I) and mesobilichrysin (II), C₃₃H₃₈O₇N₄, m.p. 240° (decomp.) when rapidly heated or m.p. 231° after changing in colour from 170° to 215° when slowly heated. (II) shows a band at 416 mμ. in ammoniacal solution. Addition of Zn(OAc)₂ to (II) in EtOH causes an immediate deepening of colour but no further change if the solution is kept in a vac. On exposure to air oxidation to (I) occurs. The colour of an alkaline solution of (II) is discharged by Na-Hg and the leuco-compound

thus produced is quickly oxidised by air and gives a urobilinoid pigment which shows an intense green fluorescence with $\text{Zn}(\text{OAc})_2$; the absorption spectrum displays a band in the blue-green; mesobilinogen behaves similarly. Biliverdin is oxidised analogously to *bilichrysin*. The chrysin may be distinguished from the urobilinoid pigments immediately by the absorption spectra and by the Zn reaction; from the rubins by the Gmelin and by the Zn reaction; from dihydromesobilirubin by the diazo-reaction; from hydroxylated as well as from non-hydroxylated dipyrromethenes by the Zn reaction (the former do not yield fluorescent Zn salts, the latter afford Zn salts somewhat similar to urobilinoid pigments). H. W.

Syntheses of isooxazole derivatives by means of fulminic acid. I. A. QUILICO and G. SPERONI (Gazzetta, 1939, 69, 508—523).—Aq. $\text{NaO}\cdot\text{N}\cdot\text{C}$ in COMe_2 containing H_2SO_4 and saturated with C_2H_2 gives 5-isopropenylisooxazole (I), b.p. 151.5—152°, which with Br in CS_2 forms 5- α -*tribromoisopropylisooxazole*, b.p. 130—135°/12 mm. With $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ (I) gives isooxazole-5-carboxylic acid; with $\text{KMnO}_4\text{--H}_2\text{SO}_4$, 5-acetylisooxazole, which with MgMeI gives 5-isooxazolyldimethylcarbinol, b.p. 90—105°/15 mm., reconverted by P_2O_5 into (I). $[\text{R}]_D$ of (I) and other isooxazoles is tabulated. E. W. W.

isooxazole group. VII. Primary alcohols and aldehydes. A. QUILICO and L. PANIZZI (Gazzetta, 1939, 69, 536—546).—3-Methylisooxazoly-5-methylamine hydrochloride and NaNO_2 give 3-methylisooxazoly-5-carbinol, b.p. 140°/25 mm. (Bz, m.p. 53—54.5°, and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}$, m.p. 82—83°, derivatives). This is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ to the acid, but when dissolved in dil. $\text{K}_2\text{Cr}_2\text{O}_7$ and dropped into boiling dil. H_2SO_4 through which steam is passing, gives 3-methylisooxazole-5-aldehyde (I), m.p. 47—48°, b.p. 70—75°/30 mm. [*peroxide*, $[\text{R}\cdot\text{CH}(\text{OH})\cdot\text{O}]_2$, m.p. 100—102° (decomp.), obtained by extracting (I) with Et_2O containing peroxide] [*p-nitrophenylhydrazone*, m.p. 258—259° (decomp.); *semicarbazone*, m.p. 225—226° (decomp.); *oxime*, m.p. 96.5—98°]. With CH_2N_2 , (I) gives 5-acetyl-3-methylisooxazole (*p-nitrophenylhydrazone*, m.p. 222—223°; *semicarbazone*, m.p. 203—204°; *oxime*, m.p. 114—115°). Similarly 5-methylisooxazoly-3-carbinol, b.p. 134.5—135.5°/30 mm. (Bz, m.p. 62—63°, and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}$, m.p. 92—93°, derivatives), is oxidised to 5-methylisooxazole-3-aldehyde, b.p. 65—75°/30 mm. [*p-nitrophenylhydrazone*, m.p. 228—229° (decomp.); *semicarbazone*, m.p. 202—203° (decomp.); *oxime*, m.p. 113—114°] (further oxidised to the acid), which with CH_2N_2 gives 3-acetyl-5-methylisooxazole (new prep. from the 3-nitrile and MgMeI). Both aldehydes in 20% KOH undergo the Cannizzaro reaction. Certain derivatives of the above position-isomerides give no depression of m.p. when mixed. E. W. W.

Morpholine condensations. C. B. KREMER, M. MELTSNER, and L. GREENSTEIN (J. Amer. Chem. Soc., 1939, 61, 2552).—Morpholine, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, and anhyd. Na_2CO_3 give 1-*o*-, m.p. 40—41°, and 1-*p*-nitrophenylmorpholine, m.p. 149—150° (also obtained from 1-phenylmorpholine by $\text{HNO}_3\text{--H}_2\text{SO}_4$). SnCl_2 then yields 1-*p*- and 1-*o*-aminophenylmorpholine, m.p. 98—98.5°. R. S. C.

Orientation of nuclear methylation in phenols and naphthols. W. T. CALDWELL and T. R. THOMPSON (J. Amer. Chem. Soc., 1939, 61, 2354—2357).—Contrary to general assumptions, $\text{CH}_2\cdot\text{NR}_2$ introduced by CH_2O and NHR_2 into a phenol may enter the position *o*- or *p*- to the OH according to rules not yet understood. Structures of the products are proved by hydrogenating-fission to PhMe derivatives. The following are prepared (many m.p. are new): 3-1'-piperidinomethyl-*p*-, m.p. 44.5—45°, and 4-1'-piperidinomethyl-*m*-cresol, an oil; 4-1'-piperidinomethyl-*s*-*m*-xyleneol, m.p. 99°; 6-1'-piperidinomethyl-4-isopropyl-*m*-cresol, m.p. 152—153°; 2-1'-piperidinomethyl- α -naphthol, m.p. 137°; 1-1'-piperidinomethyl- β -naphthol, m.p. 93—94°; 4-1'-piperidinomethyl-2:5-dimethylphenol, m.p. 130—131°; α -1'-piperidinomethylcarvacrol, m.p. 184—185°; 3:5-di-1'-morpholinomethylpyrocatechol, m.p. 173—174°; 4-1'-morpholinomethyl-*s*-*m*-xyleneol, m.p. 96.5—97°; 6-1'-morpholinomethyl-2:3:5-trimethylphenol, m.p. 78°; *x*-methylcarvacrol, b.p. 244—246°. It is established that $\text{CH}_2\cdot\text{NR}_2$ enters the 2 and 5 positions of quinol and *p*- to the OH of thymol. R. S. C.

Use of morpholine for the production of "Mannich" bases. R. H. HARRADENCE and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 72, 233—248).— COMe_2 , morpholine hydrochloride (I), and paraformaldehyde in boiling abs. EtOH give α -morpholinobutan- γ -one hydrochloride, m.p. 149° (corresponding *picrate*, m.p. 114°). The free base (II), b.p. 116°/20 mm. (considerable decomp.), is reduced by Al-Hg in moist Et_2O to α -morpholinobutan- γ -ol (III), b.p. 95—100°/2.5 mm. (*picrate*, m.p. 142—144°). (III) is converted by BzCl in CHCl_3 into α -morpholino- γ -benzoyloxybutane hydrochloride, m.p. 152° (corresponding *picrate*, m.p. 147°). α -Morpholino- γ -*p*-nitrobenzoyloxybutane hydrochloride, m.p. 199°, and the corresponding *picrate*, m.p. 211°, are described. Successive treatments of (II) with MeI and $\text{CHNa}(\text{CO}_2\text{Et})_2$ lead to *Et* 8-keto- α -carbethoxyhexoate, b.p. 162—164°/26 mm. (*semicarbazone*, m.p. 118°; *dinitrophenylhydrazone*, m.p. 55°), which does not give a colour with FeCl_3 and is hydrolysed and decarboxylated to γ -acetylbutyric acid; the ester is not cyclised by NaOEt--EtOH . *cyclo*Hexanone, (I), and 40% CH_2O readily yield 2-morpholinomethylcyclohexanone hydrochloride, m.p. 128° (corresponding *picrate*, m.p. 135°); the free base, b.p. 145—147°/5.5 mm., is reduced [$\text{Al}(\text{OPr}^i)_3$ in Pr^iOH] to 2-morpholinomethylcyclohexanol, b.p. 120—128°/1.8 mm., probably a mixture of stereoisomerides, which gives a non-cryst. *picrate*. 2-Morpholinomethyl-1-benzoyloxy-cyclohexane hydrochloride, m.p. 211°, and the corresponding *p*-nitrobenzoyl compound, m.p. 233°, are described. Analogously, 4-methylcyclohexanone yields 4-methyl-2-morpholinomethylcyclohexanone, b.p. 131—132°/2.2 mm. (*hydrochloride*, m.p. 145°; *picrate*, m.p. 139°), and 2-morpholinomethylcyclohexanol, b.p. 135—137°/2 mm. (no *picrate*; *hydrochlorides*, m.p. 228—230° and 242—244° respectively of the Bz and *p*-nitrobenzoyl derivatives). 2-Methylcyclohexanone gives 2-methyl-6-morpholinomethylcyclohexanone, b.p. 130°/1.8 mm., m.p. 48—50° (*picrate*, m.p. 118°), and 2-methyl-6-morpholinomethylcyclohexanol, b.p. 137—138°/2.3 mm.

(non-cryst. benzoate hydrochloride; *p*-nitrobenzoate hydrochloride, m.p. 237°). cyclopentanone yields 2-morpholinomethylcyclopentanone, b.p. 115—118°/2 mm. (hydrochloride, m.p. 137°; picrate, m.p. 130°), reduced by Ponndorff's method to a liquid which yields morpholine when distilled in a vac. or, under other conditions, 2:5-dimorpholinomethylcyclopentanone dihydrochloride, m.p. 195° (corresponding dipicrate, m.p. 152°. CPhMe gives *Ph* β -morpholinoethyl ketone (hydrochloride, m.p. 177°; picrate, m.p. 194°), transformed by NHPH·NH₂ into 1:3-diphenylpyrazoline, m.p. 153°. 2-Acetylthiophen affords non-cryst. 2-thienyl β -morpholinoethyl ketone (hydrochloride, m.p. 194°; picrate, m.p. 189—190°), converted by NHPH·NH₂ into 1-phenyl-3:2-thienylpyrazoline, m.p. 103°. Acetoveratrone forms 3:4-dimethoxyphenyl β -morpholinoethyl ketone, m.p. 129° (hydrochloride, m.p. 192°; picrate, m.p. 165°), which yields 1-phenyl-3:3':4'-dimethoxyphenylpyrazoline, m.p. 130°. Morpholinomethylantipyrine, m.p. 131°, and its picrate, m.p. 190°, are described. H. W.

New method of introducing the cyano-group into compounds containing methylene with mobile hydrogen. C. MUSANTE (Gazzetta, 1939, 69, 523—535).—CO₂Et·CCl₃·N·OH (I) and compounds of type CHNa(COR)₂ etc. give esters of isooxazole acids which lose CO₂ with ring-opening to form compounds of type CN·CH(COR)₂ etc. Thus (I) and CHAc₂Na give a product (II) which on hydrolysis by EtOH·KOH and acidification yields CHAc₂·CN. The product from (II) and 10% aq. KOH when acidified and treated with NHPH·NH₂ forms 3'-keto-2'-phenyl-5:6'-dimethyl-2':3'-dihydropyridazino-4':5':3:4-isooxazole, $\text{N}^{\text{N}}\text{CMe}-\text{CH}-\text{CMe} \rightarrow \text{O} (?)$, m.p. 178—179°. Similarly CHBzAcNa with (I) gives CHBzAc·CN; CHBzNa gives CHBz₂·CN; CHBzNa·CO₂Et gives CH₂Bz·CN. CN·CHNa·CO₂Et (III) and (I) in MeOH give a product which with aq. KOH and acid forms carbomethoxycyanoacetamide, m.p. 119° (decomp.) [*p*-nitrobenzeneazo-derivative, m.p. 207—209° (sinters 190°)]. (III) and (I) in EtOH give a product hydrolysed to carbethoxycyanoacetamide, m.p. 162°, also obtained from CN·CHNa·CO·NH₂ and ClCO₂Et. At 180° these substances decompose to products, m.p. <270°.

E. W. W.

Derivatives of chromanone. R. H. HARRADENCE, G. K. HUGHES, and F. LIONS (J. Proc. Roy. Soc. New South Wales, 1939, 72, 273—283).—Chromanone (I) and NHPH·NH₂ at 100° give the very unstable chromanonephenylhydrazine (II), m.p. 84° (hydrochloride, decomposes when heated), which could not be cyclised to a chromenoindole by conc. HCl, HCl·EtOH, 10% H₂SO₄, or AcOH, the product being usually a dark, red-brown oil. Chromanonedinitrophenylhydrazine has m.p. 244°. Chromanoneketazine, m.p. 176°, is completely hydrolysed to (I) by boiling HCl (1:1) and could not be converted into a pyrrole derivative by the method of Perkin and Plant. The failure of (II) to effect an indole ring-closure is not due to lack of reactivity of CH₂ vicinal to CO since (I) readily condenses with *o*-NO₂·C₆H₄·CHO to 3-*o*-nitrobenzylidenechromanone,

m.p. 142°, which can be reduced to chromeno-3':4':2:3-quinoline, m.p. 124° (picrate, m.p. 229°), more readily obtained by the action of NaOH on (I) and *o*-NH₂·C₆H₄·CHO in boiling EtOH. In the Mannich reaction (I) behaves as a normal ketone, reacting with morpholine hydrochloride and paraformaldehyde in abs. EtOH to give 3-morpholinomethyl-4-chromanone (II), m.p. 93° (hydrochloride, m.p. 171—172°; picrate, m.p. 172°), and a *by-product*, C₂₀H₁₈O₅, m.p. 167° (dinitrophenylhydrazine, m.p. 221°). Reduction of (II) with Al(OPrⁱ)₃ and PrⁱOH gives the non-cryst. 3-morpholinomethyl-4-chromanol, b.p. 175—180°/0.8 mm. (benzoate hydrochloride, m.p. 177°; *p*-nitrobenzoate hydrochloride, m.p. 195°). 3-Morpholinomethyl-4-chromanone methiodide, m.p. 149—150°, from the components in boiling EtOH, and CHAcNa·CO₂Et in boiling EtOH afford (I) and 9-keto-7:8:9:12-tetrahydroadipicpyran, m.p. 128—130° [dinitrophenylhydrazine, m.p. 250—251° (decomp.)], which gives an amorphous powder when reduced (Clemmensen). NHEt₂·HCl, paraformaldehyde, and (I) in boiling EtOH yield 3-diethylaminomethylchromanone hydrochloride, m.p. 124°. 3-N-Piperidinomethylchromanone is a liquid, b.p. 116—117°/1 mm. H. W.

Thiazoles. XXIII. Synthesis of benzthiazoles structurally related to quinoline antimalarials. H. H. FOX and M. T. BOGERT (J. Amer. Chem. Soc., 1939, 61, 2013—2017; cf. A., 1936, 869).

—OMe·C₆H₃ $\begin{smallmatrix} \text{SCI} \\ \text{N} \end{smallmatrix}$ S (modified prep. from *p*-OMe·C₆H₄·NH₂ and S₂Cl₂) with NaOH·Na₂S₂O₄ gives 4:1:2-OMe·C₆H₃(NH₂)·SNa (I), converted by dil. AcOH, followed by HCl·Et₂O, into 2-thiol-*p*-anisidine hydrochloride (NH₂ = 1) (II), m.p. 210—211° (decomp.); the Zn salt with air and aq. NH₃ gives di-2-amino-5-methoxyphenyl disulphide, m.p. 73—73.5°, and with boiling HCO₂H containing a little AcOH and Zn gives 5-methoxybenzthiazole (III), m.p. 72.5—73°, also obtained less well from (II) by HCO₂H. H₂SO₄·HNO₃ (*d* 1.45) or fuming HNO₃·H₃PO₄ converts (III) into the 6-NO₂-derivative (IV), m.p. 202—203.5°; fuming HNO₃·H₂SO₄ at 45° gives a (?) 5:7-(NO₂)₂-derivative, m.p. 161—162.5°. Fe·HCl reduces (IV) to 6-amino-5-methoxybenzthiazole, m.p. 130.5—131.5° [hydrochloride, m.p. 223—224° (decomp. after darkening; sealed tube)], and thence converted by Cl·[CH₂]₂·NEt₂·HCl in abs. EtOH at 110° into 6- β -diethylaminoethylamino-5-methoxybenzthiazole, b.p. 140—145°/0.0001 mm. BzCl·NaOH and (I) give 4:1:2-OMe·C₆H₃(NHBz)·SBz, m.p. 162—163°, converted by Ac₂O·NaOAc into 5-methoxy-1-phenylbenzthiazole (V), m.p. 114—114.5°, the 6-NO₂-derivative (VI), m.p. 210—211°, of which, prepared by AcOH·HNO₃ (*d* 1.4) at 60°, is also obtained from (IV) by BzCl·NaOH. Boiling 48% HBr hydrolyses (V) to 5-hydroxy-1-phenylbenzthiazole, m.p. 227—227.5° [(? 5:7-(NO₂)₂-derivative, m.p. 194.5—196°], the 6-NO₂-derivative, m.p. 171°, of which (prep. by warm HNO₃·AcOH) is also obtained from (VI) by boiling 10% NaOH. 1-Chloro-4-nitro-6-methoxyisobenz-1:2:3-dithiazole, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{SCI} \\ \text{NO}_2 \end{smallmatrix} \text{S}$, m.p. 220° (decomp. after darkening; slow heating) or

>190° (decomp.; rapid heating), is hydrolysed by H₂O to the 1-OH-compound, decomp. 162.5°, which yields 1:3:4:5-OMe-C₆H₂(NO₂)(NH₂)-SNa (VII) and thence the corresponding Zn salt. The thiol is obtained from (VII) by HCl, but rapidly oxidises in air to *di*-3-nitro-2-amino-5-methoxyphenyl disulphide, m.p. 171°. Addition of HCO₂H-Ac₂O to crude (VII) in H₂O gives 3-nitro-5-methoxybenzthiazole, m.p. 150—152° (lit., 149—150°), reduced by Fe-HCl to the 3-NH₂-compound, m.p. 145.5—146° (lit., 151°) [hydrochloride, m.p. 207—209° (lit., 206—208°)], and thence giving 3-β-diethylaminoethylamino-5-methoxybenzthiazole, b.p. 215—217°/5—6 mm. Warm Ac₂O converts (VII) into 3-nitro-5-methoxy-1-methylbenzthiazole, m.p. 147° (lit., 149—150°). M.p. are corr.

R. S. C.

Sulphanilamido-derivatives of heterocyclic amines. R. J. FOSBINDER and L. A. WALTER (J. Amer. Chem. Soc., 1939, 61, 2032—2033).—2:6-Diaminopyridine and *p*-NO₂-C₆H₄-SO₂Cl in EtOAc at room temp. give 2-amino-6-*p*-nitrobenzenesulphonamidopyridine, m.p. 228—230°, reduced by Sn-HCl to 2-amino-6-*p*-sulphanilamidopyridine*, m.p. 204—206°, which is also obtained from 2-amino-6-N⁴-acetylsulphanilamidopyridine, double m.p. 194—196° and 237—239° (decomp.), by hot 5—10% NaOH (10% HCl gives mainly *p*-NH₂-C₆H₄-SO₃H). Similarly are obtained 2-*p*-nitrobenzenesulphonamido-4-methylthiazole, m.p. 197—199°, 2-N⁴-acetylsulphanilamido-thiazole, m.p. 256—257°, and 4-methylthiazole, m.p. 259—260°, and 2-sulphanilamido-thiazole*, m.p. 194—196°, and 4-methylthiazole*, m.p. 236—238°. Compounds marked * are effective against strepto- and pneumo-cocci in mice.

R. S. C.

Ergot alkaloids. XVIII. Production of a base from lysergic acid. Its comparison with synthetic 6:8-dimethylergoline. W. A. JACOBS and R. G. GOULD, jun. (J. Biol. Chem., 1939, 130, 399—405; cf. A., 1938, II, 396).—The lactam obtained from dihydrolysergic acid (A., 1938, II, 384) is catalytically hydrogenated to, among other products, 6:8-dimethylergoline, m.p. 205—212° (hydrochloride, +2H₂O, [α]_D²⁵ -30° in H₂O), the inactive form (I) of which is synthesised and gives no depression of the m.p. on admixture.

1:3-CO₂H-C₁₀H₆-NH₂·H₂SO₄, OH·CMe(CH₂·OEt)₂, PhNO₂, and H₂SO₄ at 130—140° give 3-methylbenz-2':1'-5:6-quinoline-7-carboxylic acid, m.p. 320—324° (decomp.) (hydrochloride; Et ester, m.p. 85—86°), converted by HNO₃ (*d* 1.4) boiling or (*d* 1.58) at room temp. mainly into the 3'-NO₂-derivative, m.p. 320—324° (decomp.). Fe(OH)₂ reduces this to the lactam, m.p. 288—289°, of the NH₂-acid, the methiodide, m.p. 294—296° (decomp.), of which gives the methochloride, m.p. 290—295° (decomp.), and thence (H₂-PtO₂) the 1:2:3:4-H₄-lactam, m.p. 249—250° (decomp.). Na-BuOH then gives (I), m.p. 222—223° (hydrochloride, anhyd.). 2-Methyl-5:6-benzquinoline-7-carboxylic acid similarly gives a crude NO₂-acid and thence the lactam, m.p. 319—320° (decomp.), of the 3'-NH₂-acid.

R. S. C.

Alkaloids of *Nuphar luteum*. O. ACHMATOWICZ and M. MOLLÓWNA (Rocz. Chem., 1939, 19, 493—506).—The rhizomes were extracted with aq. tartaric

acid, and the alkaloids pptd. with NH₃ were subjected to fractional vac. distillation. In this way were obtained α-nupharidine (I), C₁₅H₂₃ON, b.p. 121—121.5°/2 mm., [α]_D¹⁸ -112.1° (hydrochloride, m.p. 258—259°; hydriodide, m.p. 301—302°; methiodide, m.p. 185—187°; picrate, m.p. 165—167°; platinichloride, m.p. 245—247°; O-benzoate, an oil), and β-nupharidine, C₁₅H₂₃ON, b.p. 127—128°/2.5 mm. (hydrochloride, m.p. 269—270°; hydriodide, m.p. 273—275°; picrate, m.p. 152—153°; platinichloride, m.p. 230—232°). The alkaloids do not contain OMe or NMe; they contain one OH, a tertiary N, and a double linking. With H₂ (Pt or Pd-C catalyst) they yield dihydro-α-, an oil (hydrochloride, m.p. 240—242°; hydriodide, m.p. 301—302°; picrate, m.p. 190—192°), and -β-nupharidine, an oil (hydriodide, m.p. 279—280°).

R. T.

Organo-selenium compounds. I. Selenium diphenyl dihydroxides and diphenylselenides. C. K. BANKS and C. S. HAMILTON (J. Amer. Chem. Soc., 1939, 61, 2306—2308).—PhOR (R = OH·[CH₂]₂, OH·[CH₂]₃, OH·CHMe·CH₂, and Me) with SeOCl₂ gives *Se di*-4-β-hydroxyethylphenyl, m.p. 172°, *di*-4-γ-, m.p. 159°, and -β-hydroxy-*n*-propoxyphenyl, m.p. 147°, and *di*-*p*-anisyl, m.p. 163°, dichloride, hydrolysed by hot, aq. Na₂CO₃ to the dihydroxides, m.p. 99°, 140°, 56°, and 134°, respectively. A large excess of HNO₃ (*d* 1.5) at 0° then affords *Se* 3-nitro-4-methoxy-, m.p. 203°, -4-β-hydroxyethoxy-, m.p. 175°, -4-γ-hydroxy-*n*-propoxy-, m.p. 117°, and -4-β-hydroxy-*n*-propoxyphenyl dihydroxide, m.p. 128°, reduced by H₂-Raney Ni in EtOH at room temp./2.67 atm. to *di*-3-amino-4-methoxy-, m.p. 112° (dihydrochloride, m.p. >250°), -4-β-hydroxyethoxy-, m.p. 132°, -4-γ-, m.p. 104°, and -4-β-hydroxy-*n*-propoxy-, m.p. 128°, -phenyl selenide. The (OH)₂-dihydroxides form dinitrates. NHPhAc and SeOCl₂ in Et₂O give a 2:1 additive compound, m.p. 135°; in CHCl₃ they give *Se di*-4-acetanilide dihydroxide, m.p. 223°, reduced to *di*-4-acetanilidephenyl selenide, double m.p. 176° and 216°, which with boiling 20% HCl gives *di*-*p*-aminophenyl selenide, m.p. 117°.

R. S. C.

Structure of the protein molecule. D. L. TALMUD (Acta Physicochim., 1939, 10, 753—774).—A review of work on the structure of the protein mol. is given. Wrinch's theory (A., 1937, II, 475; III, 296) of "globular" proteins has been tested experimentally. In the "cyclol" structure, all the "openings" in the faces of a globular mol. make up a space enclosed by 12 hexagons. The side groups may reduce this opening to the size of a C₆H₆ ring. Foreign mols. in a solution of a globular protein of cross-section < that of the C₆H₆ ring will diffuse through the mol. If a reaction then occurs which is accompanied by an increase in the size of the foreign mol., then that portion of the reaction products originating inside the globular mol. will be enclosed within the mol. This has been shown to occur by converting NH₂·CH₂·CO₂Et into 2:5-diketopiperazine (I) in aq. solutions of cryst. egg-albumin and pepsin. The vol. of (I) enclosed in the globular protein mols. was almost equal to the total vol. of the protein globules. It is shown that (I) is neither adsorbed nor enclosed in the form of solution. Heavy

pepsin mols. "full of" (I) have been isolated in the cryst. form. The rate of formation of (I) is accelerated by the presence of the globular structure. A hypothesis on the nature of this catalysis is put forward, the globular protein mol. being compared with an elementary biological cell. The intra-globular osmotic pressure is considered. A. J. M.

Keto-enol tautomerism of proteins. I. Tautomerism of gelatin: potentiometric titration data. A. P. KONIKOV. **II. Tautomerism of peptides and diketopiperazines.** A. P. KONIKOV and L. M. NAZAROVA (Arch. sci. biol. U.S.S.R., 1935, 39, 497—504, 505—521).—I. Diminution in p_H of gelatin solution on treatment with alkali is reversible and depends on formation of H⁺ by enolisation of peptide linkings in polypeptides and diketopiperazines.

II. The mechanism of the enolisation of peptide linkings is examined. The process is associated with a lactam-lactim transformation and is accompanied by racemisation of NH₂-acids united in the polypeptide. CH. ABS. (p)

Mol. wt. of crystalline myogen.—See A., 1939, III, 938.

Preparation of thyroxine from casein treated with iodine. C. R. HARRINGTON and E. V. PITT RIVERS (Nature, 1939, 144, 205).—The results of Ludwig and Mutzenbecher (A., 1939, II, 369) have been confirmed. Possible mechanisms by which thyroxine is formed in these experiments are discussed.

L. S. T.

Dissociation of the hæmocyanin molecule. S. BROHULT and S. CLAESON (Nature, 1939, 144, 111—112).—The effects of different types of salts, e.g., NaCl, NH₄Cl, Na₂SO₄, and CaCl₂, and of non-electrolytes, such as glucose and CO(NH₂)₂, investigated by means of the ultracentrifuge, on the dissociation of the hæmocyanin (I) mol. in 0.08M-OAc' (p_H 5.2) and PO₄''' (p_H 6.0) buffers, are recorded. Well-defined sub-multiples of the original mol. are obtained. The dissociation effect increases with the valency of the ions. NaCl gives no components < half-mols., and the reaction ceases before all the whole mols. are dissociated. The effect is smaller with non-electrolytes. Complete reversibility can be obtained in all cases where the dissociation has given only half-mols. The dissociation of the (I) mol. is a general rather than a sp. reaction associated with a special type of compound. Certain mols. or groups have a stronger effect than others, but all types, whether charged or not, affect the dissociation of (I).

L. S. T.

Reducing groups of ovalbumin. M. L. ANSON (Science, 1939, 90, 142—143).—Oxidation of denatured ovalbumin by Fe(CN)₆''' at p_H 6.8 in presence of Duponol PC occurs at a much lower [Fe(CN)₆'''] than in absence of Duponol, and the amount of Fe(CN)₆''' formed is independent of time, temp., and concns. within wide limits. Reduction of Fe(CN)₆''' does not occur when SH groups of the denatured ovalbumin are destroyed with CH₂O or CH₂I·CO·NH₂. CO(NH₂)₂ and guanidine promote the reaction with Fe(CN)₆''', but are much less effective than Duponol. I and CH₂I·CO·NH₂, but not

Fe(CN)₆''', react with native ovalbumin. Reaction is not necessarily confined to SH groups. L. S. T.

Carbon and hydrogen determinations. Effect of pressure on lessening combustion and sweeping-out times. S. S. BRODIE (Ind. Eng. Chem. [Anal.], 1939, 11, 517—518; cf. A., 1938, II, 517).—A procedure is described for the semi-micro-analysis of org. compounds under pressure (5—10 cm. of Hg) in 25 min. Halogen is absorbed by Ag supported on asbestos. J. L. D.

Qualitative test for oxygen in organic compounds. C. V. BOWEN, J. F. BOURLAND, and E. F. DEGERING (J. Chem. Educ., 1939, 16, 295—296).—Vapours of the sample are passed through wood-C heated to dull redness, and any CO₂ formed is pptd. by aq. Ba(OH)₂. Air is first removed from the apparatus by heating PhMe or C₇H₁₆ in it.

L. S. T.

Determination of amido- and nitrile-nitrogen as ammonia. L. PALFRAY, S. SABETAY, and S. ROVIRA (Compt. rend., 1939, 209, 483—485).—The substance is heated (to the b.p.) with KOH in CH₂Ph·OH during (usually) 1 hr.; the NH₃ is removed in N₂, absorbed in H₂O, and titrated with 0.1N-H₂SO₄ (methyl-orange). Good results are obtained. It is impracticable to determine the amount of KOH used. J. L. D.

Identification of flavouring constituents of commercial flavours. VIII. Semi-micro-determination of amino-nitrogen atom in semicarbazones. J. B. WILSON (J. Assoc. Off. Agric. Chem., 1939, 22, 688—690).—A semi-micro-modification of Veibel's method (cf. A., 1937, II, 130) is detailed.

E. C. S.

Semi-micro-determination of sulphur in organic substances. A. ANGELETTI (Annali Chim. Appl., 1939, 29, 356—359).—The substance (0.02—0.03 g.) is heated in a closed tube with solid KMnO₄ and the SO₄'' produced is pptd. as BaSO₄ by excess of 0.05N-BaCl₂; standard aq. K₂CrO₄ is then added to ppt. Ba and excess of K₂CrO₄ determined iodometrically.

F. O. H.

Micro-determination of selenium in organic compounds. S. UMEZAWA (Bull. Chem. Soc. Japan, 1939, 14, 153—154; cf. A., 1929, 1323).—Se is determined in selenophen and selenophthen derivatives by catalytic oxidation (O₂-Pt) in a Pregl spiral. The products are dissolved in H₂O, boiled with HCl, and reduced with NaHSO₃, and the resulting Se is weighed.

A. LI.

Qualitative organic analysis. II. Identification of alkyl halides, aromatic nitroso-compounds, aromatic hydrocarbons, and cyclopentadiene compounds. (Miss) W. J. LEVY and N. CAMPBELL (J.C.S., 1939, 1442—1446; cf. A., 1937, II, 529).—The respective alkyl halide (bromide unless stated otherwise) and CS(NH₂)₂-EtOH, then picric acid, give: *S*-methyl- (I), m.p. 224° (from MeI), -ethyl- (II), m.p. 188° (from EtI), -propyl-, m.p. 177° (more readily from PrBr than from PrCl), -isopropyl-, m.p. 196°, -*n*-, m.p. 177° (readily from BuBr), -*iso*-, m.p. 167° (from Bu²I), and -*sec*-butyl-, m.p. 166° (from iodide; small yield); -*n*-, m.p. 154°,

-iso-, m.p. 173°, and -sec.-amyl-, m.p. 157°, -n-hexyl-, m.p. 157°, -n-heptyl-, m.p. 142°, -n-octyl-, m.p. 134°, -cetyl-, m.p. 137° (from RI), -allyl-, m.p. 155° (from RCl), - α -, m.p. 167°, and - β -phenylethyl-, m.p. 139° -o-, m.p. 222°, -m-, m.p. 205°, and -p-bromobenzyl-, m.p. 219° (from RCl), -o-, m.p. 213°, -m-, m.p. 200°, and -p-chlorobenzyl-isothiocarbamide picrate, m.p. 194°. BuI or isovaleryl chloride gives (I) (using MeOH as solvent) or (II) (using EtOH). ClCO_2Me or ClCO_2Et gives (I) or (II), respectively. Similarly prepared from the respective dibromides are: *SS*-ethylene-, m.p. 260°, -propylene-, m.p. 232° (small yield), -isobutylene-, m.p. 223° (small yield), and -trimethylene-diisothiocarbamide picrate, m.p. 229°. The respective aromatic C-NO-compound and 2-phenylindole in EtOH-KOH give: 3-anilo-, m.p. 154°, -m-, m.p. 148°, and -p-chloroanilo-, m.p. 157°, -m-, m.p. 169°, and -p-bromoanilo-, m.p. 154°, -m-, m.p. 136°, and -p-tolylimino-2-phenylindolenine, m.p. 146°; $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}$ gives also a compound, m.p. 215° (cf. Reissert, A., 1909, i, 435). Most suitable for identification of C-NO-compounds are the azo-compounds from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ (method: Ingold, A., 1925, i, 646): 2-, m.p. 110°, 3-, m.p. 119°, and 4-chloro-4'-bromo-, m.p. 190°, 2:4', m.p. 104°, 3:4', m.p. 126°, and 4:4'-dibromo-, m.p. 205°, 4'-bromo-3-, m.p. 82°, and 4-methyl-azobenzene, m.p. 152°, are described. 1:2:4:5- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$ (III) is not recommended as a reagent for NH_2Ar (cf. loc. cit.); 4:6-dinitro-N-phenyl-, m.p. 145°, -m-tolyl-, m.p. 150°, -m-xylyl-, m.p. 186°, and p-anisyl-m-toluidine, m.p. 139°, are recorded. 1:4:2:3:5- $\text{C}_6\text{HMe}_2(\text{NO}_2)_3$ (IV) is not so reactive as (III) with aliphatic amines. (IV) and NH_2Me give 3:5-dinitro-N-methyl-p-xylylidine. Purification by chromatographic adsorption does not affect the fluorescence (ultra-violet) of C_{10}H_8 , anthracene (V), or chrysene (all purple), pyrene (light green), or 1:2- (purple) or 2:3-benzanthracene (VI) (slight green) (cf. Dutt, A., 1930, 1345). (V) or (VI) gives also some dianthracene (not formed in dark) or 2:3-naphthoquinone (trace in dark), respectively. Hydrocarbons, highly purified or crude, viz., CH_2Ph_2 , Ph_2 , retene, fluorene, 9-phenyl-, or 1:2- or 3:4-benz-, or 1:2:5:6-dibenz-fluorene, phenanthrene, perylene, 1:2-benzanthracene, 9:10-benzphenanthrene, and fluoranthene, give characteristic colours with $\text{CHPhCl}_2\text{-H}_2\text{SO}_4$ in C_6H_6 (cf. Lippmann *et al.*, A., 1902, ii, 702). Benzopyrene, $(\text{CH}_2\text{Ph})_2$, hydrindene, (VI), or truxene, gives no characteristic colour. Quinones do not react. $p\text{-C}_6\text{H}_4(\text{NO}_2)_2$ added to Vanscheidt's reagent (A., 1935, 74) gives a reagent which affords characteristic green or blue colours with cyclopentadiene and derivatives, e.g., dicyclopentadiene, indene, fluorene, 2-nitro-, 2-bromo-, 2:7-dibromo-, 7:2- or 2:3-bromonitro-, 1:2- or 3:4-benz-, or 1:2:5:6-dibenz-fluorene, and truxene (cf. Stobbe *et al.*, A., 1927, 347). 9-Phenylfluorene, CH_2Ph_2 , CHPh_3 , $\text{CPh}_3\cdot\text{OH}$, CPh_3CH , or acenaphthene gives a negative test. 2:4:1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ is best obtained by Storrie's method (A., 1937, II, 498).

A. T. P.

Determination of alcoholic and phenolic groups. E. RAYMOND and E. BOUVETIER (Compt.

rend., 1939, 209, 439—441; cf. Sabetay, A., 1937, II, 44).—The HCl liberated when the dry substance is treated with stearyl or palmityl chloride in gently boiling, dry CCl_4 or benzine is removed with dry air, collected in H_2O , and titrated with 0.5N-NaOH. The method is applied to a variety of alcohols and phenols but fails with those insol. in the above solvents. *tert.*-Alcohols and phenols react slowly. Amines interfere with the determination; CO_2H undergoes quant. reaction and its presence must be corr. for.

J. L. D.

Determination of water in ether. R. GASPART and G. SERRURE (Bull. Soc. chim. Belg., 1939, 48, 283—292; cf. A., 1939, II, 195).—Extinction curves from 3400 to 3700 cm^{-1} for very dil. solutions of H_2O in Et_2O are recorded with a view to their use for the determination of H_2O in Et_2O .

F. J. G.

Quantitative separation of unsaturated fatty acids in fats and phosphatides.—See A., 1939, III, 1020.

Okuda's iodine method for determination of cystine. M. SATO, T. HIRANO, and T. KAN (J. Agric. Chem. Soc. Japan, 1939, 15, 783—790).—Improvements in the method (A., 1926, 190; 1929, 1191) are described. For the quant. oxidation of cystine by I the $[\text{HCl}]$ must be 0.5—1N., the temp. of the solution 0—8°, and the $[\text{KI}]$ 0.01—0.03M. When cystine is reduced there is a close relationship between the amounts of cystine, and Zn, concn. of acid, temp. during reduction, and time of reduction. 30 min. are sufficient for the reduction of 0.1 mg.-mol. of cystine at 20° using 2 g. of Zn and 60 c.c. of N-HCl. 0.5N-HCl is better than hot H_2O for washing after the reduction and decolorisation.

J. N. A.

Micro-determination of threonine. R. J. BLOCK and (Miss) D. BOLLING (J. Biol. Chem., 1939, 130, 365—374).—Threonine (I) (0.5—5 mg. in 10 mg. of NH_2 -acids) is oxidised by $\text{Pb}(\text{OAc})_4$ (1 g.) in AcOH. The MeCHO produced is removed in air and determined colorimetrically (560 m μ . filter) after reaction with $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{OH}$ in H_2SO_4 . 15 NH_2 -acids and 9 carbohydrates are shown not to interfere. If much *l*-hydroxyproline or *l*-tryptophan is present, more $\text{Pb}(\text{OAc})_4$ must be used. Alanine and serine also yield MeCHO , but only in small amount, and do not interfere appreciably unless a large excess is present. By this method it is shown that casein yields ~3.5, serum-proteins ~6.0, and gelatin 0.5—1.1% of (I).

R. S. C.

Diazo-reaction. I. Diazo-reaction in acid and alkaline media, and in alkaline medium subsequently acidified. II. Limits and significance of Gebauer-Fülneegg's modification of Pauly's diazo-reaction. III. Significance and limits of Hanke and Koessler's proposed modification in the determination of tyrosine and tyramine. M. VIALLI and V. ERSFAMER (Arch. Fisiol., 1939, 39, 1—19, 20—32, 33—41).—I. Colour reactions with $p\text{-SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ (I) in acid and alkaline media, and in the latter subsequently acidified, are tabulated for 58 compounds of histological importance. Positive results are obtained with histidine, histamine, and

tryptophan; negative with cysteine and cystine. Purine derivatives react only at high concn. The product from ascorbic acid becomes colourless when acidified. Colour changes with COMe_2 and glucose are described.

II. The method of Gebauer-Fülnegg (A., 1930, 1605) is critically examined. Diazonium salts are coupled with 36 compounds in alkaline solution, and the product is extracted with Bu^tOH , Bu^nOH , or other org. solvent. Generally, coloured products from acidic and basic substances are respectively slightly and easily sol. in Bu^tOH . The method is not suitable for distinguishing derivatives of glyoxaline from those of tyrosine (cf. *loc. cit.*).

III. The reaction of Hanke and Koessler (A., 1922, ii, 322), in which substances are treated with a diazonium salt, followed by NaOH and NH_2OH (which gives a bluish colour with certain compounds), is examined as a method for detecting phenols. The reaction is given, *inter alia*, by $\text{CH}_2\text{R}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ ($\text{R} = p\text{-OH}\cdot\text{C}_6\text{H}_4$), $\text{CH}_2\text{R}\cdot\text{CHMe}\cdot\text{NHMe}$, and $\text{CH}_2\text{R}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$ (and also by COMe_2), but not by $\text{OH}\cdot\text{CHR}\cdot\text{CHMe}\cdot\text{NHMe}$ or 3:4:1-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$. Its use in histochemistry is recommended. E. W. W.

Preparation of aniline derivatives. Hydro-sulphoiodometric determination of azo-compounds. V. INDACOCHEA Z. (Bol. Soc. Quím. Peru, 1939, 5, 124—133).—Azo-compounds (0.1—0.5 g.) such as methyl-red can be determined by addition of 10 c.c. of 11% NaHSO_3 and 3 g. of Zn powder; after shaking, 1 c.c. of AcOH is added and then 5 g. of NaHCO_3 . Excess of the $\text{Na}_2\text{S}_2\text{O}_4$ produced in the reaction is titrated with I and starch. F. R. G.

Determination of dehydrocholic acid. G. SABA (J. Biochem. Japan, 1939, 30, 61—67).—Application of the alkaline $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ reagent of Kaziro and Shimada (A., 1937, II, 500) to the colorimetric determination of 0.25—1.5 mg. of dehydrocholic acid (pure or in tissue extracts) is described. F. O. H.

Precipitation reaction between the pyridine derivatives picoline, β -picoline, and collidine and phenol derivatives. H. BERGSTERMANN, P. A. NÖCKER, and B. KRAUSKOPF (Arch. exp. Path. Pharm., 1938, 191, 55—75).—The pptg. power of the series $\text{C}_5\text{H}_5\text{N}$, α - β -picoline, and collidine increases in that order (order of decreasing hydrophilism). The phenols fall into the same series as that observed by Labes (*ibid.*, 190, 421) using other $\text{C}_5\text{H}_5\text{N}$ derivatives. For reaction partners low in residual valency substituents the degree of hydrophobism is the governing factor. Hydrophilic substituents in the phenol, e.g., NH_2 , OH , or $\text{CO}\cdot\text{NH}_2$, weaken the reaction. J. H. B.

Precipitation reactions of quinoline and quinolinimide with phenol substitution products. R. LABES, B. KRAUSKOPF, and H. BERGSTERMANN (Arch. exp. Path. Pharm., 1939, 192, 603—617).—Quinoline is a better precipitant than the $\text{C}_5\text{H}_5\text{N}$ derivatives previously examined (cf. preceding abstract). The order of activity of the phenol substituents in promoting pptn. is approx. the same as with $\text{C}_5\text{H}_5\text{N}$,

the methylpyridines, and the ethylpyridinecarboxylates. Dihydric phenols and salicylamide, however, show a sp. increase in activity. Quinolinimide gives no reaction except with NH_2 -phenols. J. H. B.

Determination of 8-hydroxyquinoline in presence of sulphosalicylic acid. A. CASTIGLIONI (Annali Chim. Appl., 1939, 29, 315—316).—The ppt. from 8-hydroxyquinoline (B) and silicotungstic acid in dil. HCl solution is dried at 105° and weighed as $12\text{WO}_3\cdot\text{SiO}_2\cdot 4\text{B}\cdot 4\text{H}_2\text{O}$ (factor 0.2039). F. O. H.

Ultramicro-determination of thiamine by fermentation.—See A., 1939, III, 920.

Boric acid colour reaction of flavone derivatives. C. W. WILSON (J. Amer. Chem. Soc., 1939, 61, 2303—2306).—The yellow colour given by citrin with H_3BO_3 and anhyd. citric acid in COMe_2 is given also by quercitrin, kaempferol, 2:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$:3:4, 5:2':4':6'-tetrahydroxy-4-methoxy- and 4:2':4':6'-tetrahydroxy-chalkone, but not by fisetin, naringenin, hesperetin, or cyanidin. Curcumin gives a pink colour. The nature of the necessary groups is discussed. R. S. C.

Determination of the barbiturates. R. F. CHATFIELD (Pharm. J., 1939, 143, 346).—The work of Paget and Tilley (A., 1937, II, 268) on the reactions of ten substituted barbiturates with Millon's reagent is modified and a proposed separation table is given. J. D. R.

Silicotungstic acid determination of nicotine. Errors involved and a new technique for steam-distillation of nicotine. A. W. AVENS and G. W. PEARCE (Ind. Eng. Chem. [Anal.], 1939, 11, 505—508).—The sample is suspended in H_2O made just alkaline [NaOH or $\text{Ba}(\text{OH})_2$] to phenolphthalein and distilled in steam (30 min.) under pressure, the distillate being collected in aq. HCl . Silicotungstic acid (I) (12%) is added to an aliquot of the distillate, which is heated (steam-bath) for 15 min. and then left overnight at 0 — 10° . The ppt. is filtered off under standard conditions and nicotine (II) determined in the usual manner. Different filter-papers retain different amounts of (I) which introduces errors into abs. determinations of (II). Under standard conditions, the amount retained is const. J. L. D.

Colorimetric determination of hydroxyproline and its application to gelatin hydrolysates. W. D. MCFARLANE and G. H. GUEST (Canad. J. Res., 1939, 17, B, 139—142).—The solution is treated with CuSO_4 , NaOH , and H_2O_2 , followed by isatin and HCl , and the red colour is determined photo-electrically using a light filter. Moisture-free gelatin contains 14.65% of hydroxyproline. S. H. H.

Colorimetric determination of proline. G. H. GUEST (Canad. J. Res., 1939, 17, B, 143—144).—The proline (I) in casein (II) is determined by oxidation of (I) with PbO_2 and condensation of the product with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ to give a red compound, estimated photo-electrically. (II) contains 7.94% of (I). The method fails in presence of hydroxyproline. S. H. H.

A., II.—Organic Chemistry

DECEMBER, 1939.

Separation of organic compounds containing oxygen from their mixtures with hydrocarbons. A. S. OSOKIN (J. Gen. Chem. Russ., 1939, 9, 1315—1325).—Alcohols, aldehydes, ketones, esters, and acid anhydrides are pptd. from their solutions in light petroleum by dry $MgCl_2$. If a mixture of hydrocarbons with substances containing O is present, the acids, phenols, etc. are eliminated by alkali, the rest is pptd. by $MgCl_2$, and the residue containing aromatic ethers, furan, etc. is analysed by combustion.

J. J. B.

Cadmium-photosensitised reactions of ethane.—See A., 1939, I, 620.

Isomerisation of butanes and their equilibrium ratios. B. L. MOLDAVSKI and T. V. NISOVKINA (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 919—920).—The equilibrium $n\text{-C}_4\text{H}_{10} \rightleftharpoons \text{iso-C}_4\text{H}_{10}$ has been examined in the liquid phase at 70° in presence of $AlCl_3 + CuSO_4 \cdot 2HCl$ and at 110—180° by passing the vapours, mixed with HCl, over $AlCl_3$.

H. W.

Kinetics of cyclisation of diisobutyl at platinumised charcoal catalyst.—See A., 1939, I, 618.

Polymerisation of gaseous butadiene.—See A., 1939, I, 614.

Catalysed polymerisation of butadiene at a liquid-gas interface.—See A., 1939, I, 619.

Structure of the mixed polymeride of butadiene and acrylonitrile. E. N. ALEXEEVA (J. Gen. Chem. Russ., 1939, 9, 1426—1430).—Butadiene and $CH_2=CH\cdot CN$ are heated at 60° for 116 hr. in presence of 1% of BzO_2H , and the reaction product is treated successively with O_3 and H_2O_2 . The ozonolysis products are succinic, butanetri-, hexanetra-, and dodecanepenta-carboxylic acids. These results are explicable on the assumption that the polymerisation product consists of chains of $\cdot CH_2\cdot CH\cdot CH\cdot CH_2\cdot$ and $\cdot CH_2\cdot CH(CN)\cdot$ units.

R. T.

Synthesis of piperylene from furfuraldehyde. I. A. M. BERKENHEIM and T. F. DANKOVA (J. Gen. Chem. Russ., 1939, 9, 924—931).—Piperylene was obtained from furfuraldehyde (I) by the following reactions, the yields being shown in parentheses: (I) with CH_2O and NaOH yields furfuryl alcohol (90—91%), which is converted by HCl into $CH_2Ac\cdot CH_2\cdot CO_2H$ (62—64%), reduced to γ -valerolactone by Na-Hg (81.5%), or electrolytically (88%), from which $OH\cdot CHMe\cdot [CH_2]_3\cdot OH$ is obtained by reduction with Na-EtOH in xylene (59%), converted into $CHMeBr\cdot [CH_2]_3\cdot Br$ by saturated HBr at 0°, from which a bromopentene, b.p. 127—128° (59—

60%), is obtained by heating with $NPhMe_2$ at 175—180°, converted by KOH-EtOH into $CHMe\cdot CH\cdot CH\cdot CH_2$ (60%) and an ether, $C_5H_9\cdot OEt$, b.p. 120—123° (17%).

V. A. P.

Fluorocarbons. Reactions of fluorine with carbon. J. H. SIMONS and L. P. BLOCK (J. Amer. Chem. Soc., 1939, 61, 2962—2966).— F_2 was passed direct from the generator through a Cu tube containing finely-divided C and 1% of a Hg^I or Hg^{II} salt, and heated to a dull redness. The reaction takes place steadily and without explosion and the gas, after successive treatment with aq. NaOH, H_2O , aq. NaOH, conc. H_2SO_4 , and P_2O_5 , was fractionated by means of a low-temp. fractionating column. Besides CF_4 and C_2F_6 and a mixture (of fluorocarbons) boiling from 25° to 160°, six fractions of const. b.p. have been obtained and analysed. Various physical data (m.p., b.p., ρ , v.p., heats of vaporisation) are given for these fractions, which correspond with octafluoropropane, decafluorobutane (two isomerides), decafluorocyclopentane, dodecafluorocyclohexane, tetradecafluorocycloheptane. Since their properties are not those of hydrocarbon derivatives a new nomenclature is suggested for them. The mixture (b.p. 25—160°) consists essentially of two parts, one of b.p. 25—95° probably containing fluorocarbons of from 3—8 C atoms, the other, b.p. 95—160°, probably containing fluorocarbons with 8—12 C.

W. R. A.

Halogenation of hydrocarbons. Chlorination of olefines and olefine-paraffin mixtures at moderate temperatures; induced substitution. H. P. A. GROLL, G. HEARNE, F. F. RUST, and W. E. VAUGHAN (Ind. Eng. Chem., 1939, 31, 1239—1244).—Analyses for free Cl_2 in olefine- Cl_2 mixtures are liable to error, owing to extraneous catalysed reactions in the absorption vessel. Cl may be determined, e.g., with C_2H_4 , by 10% aq. KOH at room temp. or 10% aq. KI at 80°; with C_3H_6 or $n\text{-C}_4H_{10}$, 10% aq. KOH at 80°; with Δ^a - or Δ^b - C_4H_8 , 10 or 5% aq. KOH at 80°, with diluent N_2 . Olefines react with Cl_2 (O_2 -free) only slowly, if at all, in the gas phase over clean Pyrex glass at 125—135°. Packing with Pyrex rods, or saturation of C_2H_4 with $C_2H_4Cl_2$ or H_2O , has no effect. Illumination (high-intensity Hg arc) of a non-reacting equimol. mixture of C_2H_4 and Cl_2 at 25° allows complete utilisation of Cl_2 ; once begun, reaction proceeds in absence of light, owing to presence of a liquid phase (cf. Stewart *et al.*, A., 1936, 37). If the temp. of reactor through which $C_2H_4 + Cl_2$ are flowing at 135° is lowered, no reaction occurs until 20—23°, when all the Cl_2 reacts rapidly. "Onset temp." are also recorded for the above olefines, with or without N_2 dilution; % Cl substituted

or added is given. Once started, reaction proceeds at temp. \gg onset val.; e.g., chlorination of C_2H_4 begun at 20° continues at 65° . The compositions of the products of chlorination of the olefines are recorded. In presence of O_2 , the % Cl reacting by substitution with olefines or mixtures, e.g., $C_3H_6 + C_3H_8$, $C_4H_8 + C_4H_{10}$, is decreased; substitution into the paraffin is more strongly inhibited than that into the additive product (induced reactions; Stewart *et al.*, A., 1931, 610). Even when catalysts, e.g., $CaCl_2$, are present, O_2 strongly inhibits some substitution reactions in the liquid phase. Reaction in liquid phase, once begun, is little, if at all, affected by catalyst. Catalytic vapour-phase chlorination of olefines or olefine-paraffin mixtures, e.g., $C_4H_8 + C_4H_{10}$ at 80 – 100° , occurs in absence of liquid. Concurrent substitution reactions are not inhibited by O_2 (even in large amount) and are thus due to thermal and catalytic conditions, rather than to induction. A. T. P.

Action of hexachloroethane on Grignard reagents. V. V. KORSCHAK (J. Gen. Chem. Russ., 1939, 9, 1153–1154).—The action of various Grignard reagents on C_2Cl_6 does not lead to the substitution of the Cl of C_2Cl_6 by alkyl R. The products are C_2Cl_4 , $CHCl_2 \cdot CHCl_2$, $CCl_3 \cdot CH_2Cl$, and C_2HCl_5 , the last three formed by reduction of C_2Cl_6 , with products derived from the free radical formed in the reaction $C_2Cl_6 + 2MgRBr = C_2Cl_4 + 2R + 2MgClBr$, such as C_2H_6 and C_2H_4 resulting from the disproportionation of Et. G. A. R. K.

Aliphatic chloro-derivatives. XVI. Vicinal effect. D. V. TISCHTSCHENKO (J. Gen. Chem. Russ., 1939, 9, 1380–1388).—The velocity of hydrolysis in aq. NaOH–EtOH of $(CH_2 \cdot CMe_2Cl)_2$, $CH_2(CMe_2Cl)_2$, $(CHMeCl)_2$, $(CH_2 \cdot CHMeCl)_2$, $CH_3(CHMeCl)_2$, $(CMe_2Cl)_2$, $Cl[CH_2]_4Cl$, $Cl[CH_2]_3Cl$, and $Cl[CH_2]_2Cl$ rises with increasing distance between the Cl, and falls in the order $CH_2Cl < CHMeCl < CMe_2Cl$. R. T.

Peroxide effect in the addition of reagents to unsaturated compounds. XXI. "Normal" and "abnormal" additions of hydrogen bromide. M. S. KHARASCH, S. C. KLEIGER, and F. R. MAYO (J. Org. Chem., 1939, 4, 428–435).—Study has been made of the addition of HCl and HBr to $CH_2 \cdot CHMe$, $CH_2 \cdot CMe_2$, $CH_2 \cdot CH \cdot CH_2Br$, $CH_2 \cdot CH \cdot CH_2Cl$, $CH_2 \cdot CMeBr$, $CH_2 \cdot CMeCl$, $CH_2 \cdot CHCl$, $CH_2 \cdot CHBr$, $CCl_3 \cdot CHCl$, $CHBr \cdot CHMe$, and $CHCl \cdot CHMe$ in the presence and absence of $FeCl_3$ as catalyst. The direction of addition of HCl is the same as that of the "normal" addition of HBr. Fe^{III} halides greatly accelerate the rate but do not change the "normal" direction of addition of both halogen acids. It is suggested that the "normal" addition of HBr be defined as that corresponding with the following equiv. additive reactions: the addition of HCl with or without $FeCl_3$ and the addition of HBr in the presence of $FeCl_3$. H. W.

Mechanism of the oxygen effect on hydrogen bromide reacting with ethenoid compounds. Y. URUSHIBARA and O. SIMAMURA (Bull. Chem. Soc. Japan, 1939, 14, 323–336).—In the presence of traces of O_2 , addition of HBr to $CH_2 \cdot CH \cdot CH_2Br$ gives

$CH_2(CH_2Br)_2$ exclusively. Peroxides and H_2O are formed only in presence of excess of O_2 . The reversal of the normal addition of HBr to allyl and vinyl bromides, and the isomerisation of isostilbene by HBr and O_2 , can be explained by a chain mechanism involving initial formation of Br radicals by Br atoms. L. J. J.

Aliphatic chloro-compounds. XV. Chlorination of isobutylene. I. DIAKONOV and D. TISCHTSCHENKO (J. Gen. Chem. Russ., 1939, 9, 1258–1264).— $CMe_2 \cdot CH_2$ and Cl_2 combine to give Bu^iCl , isobutenyl chloride (I), and a mixture of 40% of $CHCl \cdot CMe \cdot CH_2Cl$ and 60% of $CH_2 \cdot C(CH_2Cl)_2$, identified by ozonisation to chloro- and dichloro-acetone respectively. A similar mixture of unsaturated Cl_2 -compounds is produced by chlorination of (I) in presence of Na_2CO_3 . The production of these Cl_2 -compounds is due to an abnormal Lvov–Kondakov reaction and is less marked than with $CMe_2 \cdot CHMe$, in which steric hindrance plays a greater part in preventing the normal addition of Cl_2 to the double linking, in agreement with the theoretical considerations already put forward. G. A. R. K.

Isomeric transformations of halogen derivatives of unsaturated aliphatic hydrocarbons. II. Hydrolysis of α -chloro- γ -methylallene. T. A. FAVORSKAJA (J. Gen. Chem. Russ., 1939, 9, 1237–1242).— $CMe_2 \cdot C \cdot CHCl$ (I) when heated with H_2O and $CaCO_3$ yields γ -chloro- γ -methyl- Δ^2 -butene (II), a large amount of α -chloro- γ -methyl- Δ^2 -butadiene, a small amount of dimeric chloride $C_{10}H_{14}Cl_2$ (A., 1930, 574), and allylene (III), identified by conversion into mesityl oxide by H_2SO_4 . The formation of (III) is thought to proceed through the intermediate formation of the unstable 4-chloro-2-methyl- Δ^1 -cyclobutene, which then breaks up into (III) and vinyl chloride, this being polymerised. $\beta\beta$ -Dimethylacetaldehyde is also formed; the production of it from $OH \cdot CMe_2 \cdot C \cdot CH$ is now interpreted as an anionotropic change, similar to the formation of (I) from (II) (cf. A., 1939, II, 354). G. A. R. K.

Exchange reactions in deuteroalcohol. II. W. G. BROWN, M. S. KHARASCH, and W. R. SPROWLS (J. Org. Chem., 1939, 4, 442–455; cf. A., 1937, II, 364).—Re-investigation shows that $NPhMe_2$ does not exchange H for D in EtOH in the absence of acid. $NHPh_2$ exchanges 1 H (presumably from NH) in the absence of acid whilst in presence of acid the exchange no. is 6. The most probable val. for the no. of exchangeable H is 7 and it is therefore likely that the exchange reaction in the presence of acid involves the *ortho* and *para* positions in each ring in addition to the H of NH. NPh_3 behaves similarly, the observed exchange no., 7–9, corresponding with the exchange of 9 H. There is, therefore, no marked diminution in the ability of the nuclear H atoms to exchange which would parallel the very great decrease of basicity in the series $NPhMe_2$, $NHPh_2$, and NPh_3 ; these results provide convincing evidence against the normal salt (or ion) as an intermediate in the exchange reaction. Under the experimental conditions adopted o - $NO_2 \cdot C_6H_4 \cdot NMe_2$ exhibits no exchange. With p - $NO_2 \cdot C_6H_4 \cdot NMe_2$ 2 H are completely replaced in

presence of acid whereas with $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ the theoretical limit of 3 is not attained. The possibilities of steric hindrance and damped resonance are discussed. The alkali-catalysed exchange reaction of fluorene is representative of a different type of H lability, viz., a type in which labile H is acidic; it is found also in xanthone, indene, and 9-phenylfluorene but not in CHPh_3 , which is less acidic. The origin of the lability of H is to be sought in the cyclopentadiene nucleus, which would be converted by formation of an anion by loss of a proton into a structure in which various possibilities for resonance are present. In neutral solution 9-fluorenol exchanges 1 H whilst in presence of alkali a second H, presumably attached to C_{10} , is also replaced. In acid solution the compound decomposes rapidly to didiphenylene-ethylene. 9-Methoxyfluorene also decomposes in acid solution but no change is observed in neutral or alkaline solution. 9-Amino- and 9-dimethylamino-fluorene suffer decomp. in neutral, acid, or alkaline solution. The exchange reaction of acetomesitylene (I) takes place to a greater extent than the corresponding reaction of COPhMe , the difference being particularly noticeable in neutral solution where, under the experimental conditions adopted, the (I) change is $\sim 50\%$ complete whilst that of COPhMe is $\sim 5\%$ complete. The process of enolisation in the former, whether acid- or base-catalysed, is appreciably faster than in COPhMe . Contrary to previous observations, the exchange of 2-methylquinoline at 110° for 106 hr. corresponds with somewhat < 1 atom. The change is subject to acid catalysis. H. W.

Synthesis of an alcohol with two conjugated triple linkings. J. S. SALKIND and M. A. AIZIKOVITSCH (J. Gen. Chem. Russ., 1939, 9, 961—964).— $(\text{OH}\cdot\text{CMe}_2\cdot\text{C}\equiv\text{C})_2$, when heated with KOH , $\text{Ba}(\text{OH})_2$, or CaO , yields COMe_2 , $(\text{CH}\equiv\text{C})_2$, and ε -methyl- $\Delta^{\gamma\gamma}$ -hexadi-ene- ε -ol, b.p. $59\text{--}61^\circ/6$ mm. R. T.

Catalytic action of p -toluenesulphonic acid on acetylene γ -glycols. I. β -Dimethyl- $\Delta^{\gamma\gamma}$ -hexinene- β -diol and γ -dimethyl- Δ^8 -octinene- γ -diol. A. BABAJAN (J. Gen. Chem. Russ., 1939, 9, 1410—1411).—The glycols when heated at $140\text{--}150^\circ$ with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ give $(\text{CH}_2\cdot\text{CMe}\cdot\text{C})_2$ or $(\text{CHMe}\cdot\text{CMe}\cdot\text{C})_2$ in $> 90\%$ yield. R. T.

Synthesis of glycols of the diacetylene series. J. S. SALKIND and I. M. GVERDTZITELI (J. Gen. Chem. Russ., 1939, 9, 971—974).—Acetylenic alcohols react with CuCl and NH_4Cl in H_2O , at room temp., as follows: $\text{OH}\cdot\text{CHR}\cdot\text{C}\equiv\text{CH} \rightarrow (\text{OH}\cdot\text{CHR}\cdot\text{C}\equiv\text{C})_2$. The following were thus prepared: $\alpha\delta$ -di-(1-hydroxycyclopentyl)- $\Delta^{\gamma\gamma}$ -butadi-ene, m.p. $132\text{--}134.2^\circ$ [hydrogenated (Pt-black) to $\alpha\delta$ -di-(1-hydroxycyclopentyl)ethane, m.p. $91.8\text{--}92.5^\circ$], $(\text{OH}\cdot\text{CHMe}\cdot\text{C}\equiv\text{C})_2$, Δ^{en} -dodecadi-ene- δ_1 : 9-diol, b.p. $159\text{--}162^\circ/7$ mm., and $\alpha\zeta$ -di-phenyl- Δ^{B} -hexadi-ene- $\alpha\zeta$ -diol, m.p. $132\text{--}133^\circ$. R. T.

Preparation of ethers. P. G. STEVENS and S. A. V. DEANS (Canad. J. Res., 1939, 17, B, 290—292).—The Na derivative of C_{10}H_8 or Ph_2 prepared in $(\text{CH}_2\cdot\text{OMe})_2$ according to Scott *et al.* (A., 1937, II, 55) is cooled and the intensely coloured solution is treated gradually with the alcohol (I) which is to be converted into its Me ether. The colour disappears

when one equiv. of (I) has been added. MeI or Me_2SO_4 is added slowly, keeping the solution at $> 20^\circ$, and the mixture is kept overnight. If the ether has a low b.p. Me_2SO_4 is used and the products can be fractionally distilled directly. If it has a high b.p. MeI is used and the mixture is treated with H_2O and the product extracted with Et_2O , dried, and distilled. In some cases the hydrocarbon can be removed by distillation with steam. Alcohols of lower mol. wt. give less satisfactory results owing to manipulative losses. The difficulties may be partly overcome by use of Me_2O as solvent, thus avoiding the separation of $\text{CH}_2\cdot\text{CH}\cdot\text{OMe}$ formed by cleavage of $(\text{CH}_2\cdot\text{OMe})_2$. OH-compounds with other functional groups, e.g., $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, can be etherified in this manner by merely reversing the process of addition. The yields are lower but about equal to those obtained by Purdie's method. Optically active alcohols yield ethers of high rotatory power. The process has been applied to $\text{Pr}^{\text{B}}\text{OH}$, $\text{Bu}^{\text{B}}\text{OH}$, $\text{CHMeBu}\cdot\text{OH}$, linalool, cholesterol, and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$. H. W.

Ether peroxides. M. S. KHARASCH and M. GLADSTONE (J. Chem. Educ., 1939, 16, 498).—Triacetone peroxide (I) has been isolated from an old sample of $\text{Pr}^{\text{B}}_2\text{O}$. (I) explodes on rubbing or heating, and with diacetone peroxide may be responsible for the explosions during the distillation of old $\text{Pr}^{\text{B}}_2\text{O}$ (A., 1936, 1091). L. S. T.

Isomerisation of geranyl acetate. V. I. ISAGULIANTZ and G. A. SEREBRENNIKOV (J. Gen. Chem. Russ., 1939, 9, 917—923).—Geranyl acetate (I) and 85% H_3PO_4 at -5° give cyclogeranyl acetate (22% yield) + terpin hydrate + an alcohol, b.p. $174\text{--}175^\circ$. (I) and 92% H_3PO_4 at -5° yield 36% of cyclo-isomeride. Cyclisation is not effected by ZnCl_2 , ZnBr_2 , $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, or HCO_2H . cycloGeranyl butyrate, b.p. $106^\circ/6$ mm., and hexoate, b.p. $126^\circ/5$ mm., are described. V. A. P.

X-Ray and thermal examination of glycerides. VII. Unsymmetrical mixed triglycerides, $\text{COR}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{COR})\cdot\text{CH}_2\cdot\text{O}\cdot\text{COR}'$. M. G. R. CARTER and T. MALKIN (J.C.S., 1939, 1518—1521; cf. A., 1939, II, 403).—The following unsymmetrical triglycerides have been prepared by the methods used previously (A., 1939, II, 97) and all exist in four solid modifications, vitreous, α , β' , and β , the m.p. being given in that order; α -decodimyrustin (15° , 32° , 38° , 43.5°), α -laurodipalmitin (32° , 45° , 49.5° , 54°), α -myristodistearin (44° , 54° , 57.5° , 62°), α -myristodidecain (3° , 20° , 31° , 34.5°), α -palmitodilaurin (20° , 33° , 43° , 46.5°), α -stearodimyrustin (36° , 46° , 52° , 56°), α -decodipalmitin (23° , 37° , 41° , 45.5°), α -laurodistearin (36° , 47° , 52° , —), α -palmitodidecain (2° , 24° , 32° , 35°), α -stearodilaurin (20° , 31° , 41.5° , 45°), α -stearodidecain (13° , 32° , 38° , 41°), α -decodistearin (33° , 42.5° , 46° , 49°). Long spacings of the above, with the exception of the first three, correspond with twice the length of a single mol., but side spacings are of the normal type. The importance of the X-ray method in the identification of natural glycerides is discussed. J. D. R.

Reaction between the oxides of olefines and sulphur monochloride. M. S. MALINOVSKI (J.

Gen. Chem. Russ., 1939, 9, 832—839).— $(\text{CH}_3)_2\text{O} + \text{S}_2\text{Cl}_2$ yield S, $(\text{CH}_2\text{Cl})_2$, CHMeCl_2 , $\text{CH}_2\text{Cl}\cdot\text{CHO}$, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$, and $(\text{Cl}\cdot[\text{CH}_2])_2\text{SO}_3$. Propylene oxide and S_2Cl_2 yield S, $\beta\beta'$ -dichlorodipropyl sulphite, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}$, and $\text{CHMeCl}\cdot\text{CHO}$. Epichlorohydrin and S_2Cl_2 when heated give S, $\text{OH}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$, and $\text{CO}(\text{CH}_2\text{Cl})_2$. V. A. P.

Xanthates. I. Reactions of some xanthic acids with metallic [salts]. K. ATSUKI and T. TAKADA (J. Cellulose Inst. Tokyo, 1939, 15, 321—327).—Me, Et, Pr, Bu, amyl, and CH_2Ph xanthates and 48 metal xanthates have been prepared from the appropriate alkoxides and hydroxides or by double decomp. between the Na xanthate and a metallic salt. The yield decreases with increasing valency of the metal, and the most stable compound is that containing the metal in its lowest valency state. The colour is characteristic of the metal, not of the alcohol, but is not the same as that of the corresponding metallic sulphide. Xanthates of univalent metals are insol. and those of multivalent metals are sol. in Et_2O . The solubility in H_2O decreases with increasing mol. wt. of the alcohol. Cellulose xanthates are similar to other xanthates containing the same metal, but owing to their high mol. wt. they decompose readily, and the decomp. products affect the colour. W. A. R.

Reaction of sodamide with salts of organic acids. L. C. FREIDLIN and A. I. LEBEDEVYA (J. Gen. Chem. Russ., 1939, 9, 996—1006).— NaNH_2 and salts of carboxylic acids react as follows: $\text{R}\cdot\text{CO}_2\text{M} + \text{NaNH}_2 \rightarrow \text{NH}_2\cdot\text{CR}(\text{ONa})\cdot\text{OM} \rightarrow \text{MOH} + \text{NH}_2\cdot\text{CR}\cdot\text{ONa} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NHNa} (+ \text{NaNH}_2) \rightarrow \text{NH}_2\cdot\text{CR}(\text{NHNa})\cdot\text{ONa} \rightarrow \text{NaHCN}_2 + \text{NaOH} + \text{RH}$; $\text{R}\cdot\text{CO}_2\text{M} + \text{MOH} \rightarrow \text{M}_2\text{CO}_3 + \text{RH}$ ($\text{R} = \text{H, Me, Et, Ph}$). With dibasic acids the reactions are: $\text{Na}_2\text{C}_2\text{O}_4 + 2\text{NaNH}_2 \rightarrow \text{NaHCN}_2 + \text{Na}_2\text{CO}_3 + \text{NaOH} + \text{H}_2$, and $(\text{CH}_2\cdot\text{CO}_2\text{Na})_2 + 2\text{NaNH}_2 \rightarrow \text{NaHCN}_2 + \text{NaCN} + \text{Na}_2\text{CO}_3 + \text{NaOH} + \text{CH}_4 + 2\text{H}_2$. R. T.

Electrolysis of mixtures of pivalates with nitrates. F. FICHTER and R. GUNST (Helv. Chim. Acta, 1939, 22, 1300—1307).—The identified products of the electrolysis of the mixture are $\text{Bu}^v\text{O}\cdot\text{NO}$, Bu^vOH , $\text{CMe}_2\cdot\text{CH}_2$, $\text{NO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{NO}_2$, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ (dicarbanilide, m.p. 138°), Bu^v pivalate, $\text{OBu}^v\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{ONO}_2$, and $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OBu}^v$. The formation of alkyl nitrate is not observed. It therefore appears that these are not formed from intermediate alkenes but that the simple members are derived from alcohol and HNO_3 and their homologues from the simpler compounds and alkenes. Glycol dinitrates with the simple or multiple mol. wt. of the hydrocarbon residue are formed from the alkene and electrolysed HNO_3 . H. W.

Oxidation of stearic acid by oxygen.—See A., 1939, I, 619.

Effect of periodic acid on lactic acid and its degradation products (acetaldehyde, methyl alcohol, formaldehyde, formic acid). P. FLEURY and R. BORISSON (J. Pharm. Chim., 1939, [viii], 30, 145—162; cf. A., 1937, II, 273).—Lactic acid (I) with HIO_4 in $\text{N}\cdot\text{H}_2\text{SO}_4$ at 100° (sealed tube) in 16

days is oxidised completely to CO_2 and H_2O as shown by the disappearance of HIO_4 (cf. A., 1933, 486). The rate of reaction increases with the temp., the acidity, and with increasing amounts of HIO_4 . After 1 atom of O is used per mol. of (I), the reaction rate increases (especially under acid conditions) until 4 O per mol. is reached, the utilisation of O_2 then becoming very low. The initial reaction (1 hr.) in which 1 O is utilised per mol. of (I) liberates CO_2 and MeCHO quantitatively if the latter is removed as it is formed. MeCHO under similar conditions requires 5 O for complete oxidation, the factors governing the rate of reaction being similar to those for (I). The rates of oxidation of MeCHO determined by a reduction method (cf. Malaprade, A., 1934, 1090) and by the rate of disappearance of HIO_4 do not agree, because CH_2O which is identified in the reaction product after 13.5 hr. is an intermediate degradation product. HCO_2H and MeOH are also identified. HCO_2H , CH_2O , and MeOH are oxidised under similar conditions to CO_2 and H_2O .

J. L. D.

Catalytic hydrogenation of the oxides of unsaturated acids. G. V. PIGULEVSKI and Z. J. RUBASCHKO (J. Gen. Chem. Russ., 1939, 9, 829—831).—Catalytic hydrogenation (Pd-black in abs. EtOH at room temp.) of the oxide of Et oleate (new m.p. 21°) leads to rupture of the oxide ring with formation of Et α -hydroxystearate. V. A. P.

Diethyl methylenemalonate. G. B. BACHMAN and H. A. TANNER (J. Org. Chem., 1939, 4, 493—501).—Yields between 4% and 17% of Et_2 methylenemalonate (I) are obtained when $\text{CH}_2(\text{CO}_2\text{Et})_2$ and CH_2O [as formalin, paraformaldehyde (II), or a solution of CH_2O in the ester] are passed over AlPO_4 , glass wool, soda-lime, Al_2O_3 , Na_3PO_4 , Na_2HPO_4 , or $\text{Ca}_3(\text{PO}_4)_2$ at temp. varying from 250° to 420° . (I), b.p. $210^\circ/760$ mm., is obtained in 40% yield by heating a mixture of $\text{CH}_2(\text{CO}_2\text{Et})_2$ (II), $\text{Ca}(\text{OAc})_2$, and KOAc in glacial AcOH at 100° until a clear solution is obtained and then distilling the product under diminished pressure. Impure (I) polymerises only with difficulty. The ease with which freshly prepared (I) polymerises is probably due to the presence in it of acrylic acid or Et acrylate, both of which polymerise with great ease and are capable of initiating the polymerisation of (I). The polymeride obtained from highly purified (I) is a colourless, transparent glass which changes rapidly to a hard but brittle porcelain-like solid. It dissolves slowly in AcOH , COMe_2 , or EtOH and is pptd. by H_2O or light petroleum as a white, granular powder. It decomposes at 230 — 240° to the monomeride and products of high b.p. It co-polymerises with butadiene to Et_2 Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. $117^\circ/6$ mm., with β -methylbutadiene to Et_2 3-methyl- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. $127^\circ/6$ mm., with $\beta\gamma$ -dimethylbutadiene to Et_2 3:4-dimethyl- Δ^3 -cyclohexene-1:1-dicarboxylate, b.p. $136^\circ/6$ mm. [acid, m.p. 186.5 — 188° (decomp.), decarboxylated to 3:4-dimethyl- Δ^3 -cyclohexene-1-carboxylic acid, m.p. 80 — 81°], and with anthracene to a compound, m.p. 126 — 127° . (I) does not resemble maleic anhydride (II) in the ease or completeness of its co-polymeris-

ation with other olefines. Also there is no apparent tendency to form co-polymerides in a definite ratio with other unsaturated substances. The films obtained from (I) and vinyl acetate, Me methacrylate, Me₂ itaconate, styrene, and Et vinyl ether in presence of Bz₂O₂ are described. (I) does not appear to react with (II) or Me isopropenyl ketone under these conditions. H. W.

Ethyl hydrogen methyldiglycolates. P. VIELES and M. AMIR (Compt. rend., 1939, 209, 457—459).—*dl*-Methyldiglycolic anhydride with EtOH gives *Et H dl-methyldiglycolate* (I), b.p. 168—170°/20 mm. Partial saponification of the Et ester of (I) gives (I) and probably some *Et H dl-methyldiglycolate* (II), b.p. 168—170°/20 mm., which is more rapidly esterified than (I). (I) with excess of boiling MeOH and a little CuSO₄ gives Me *Et dl-methyldiglycolate*, b.p. 126—128°/25 mm., [α]_D²⁵₄₀₁ —12.6° (cf. A., 1936, 823). J. L. D.

Chloralides. Condensation of butylchloral with α -hydroxycarboxylic acids. N. M. SHAH (J. Indian Chem. Soc., 1939, 16, 285—286; cf. A., 1934, 869).—Citric, malic, and tartaric acids with CHMeCl·CCl₂·CHO·H₂O in conc. H₂SO₄ give their respective *butylchloralides*, CHMeCl·CCl₂·CH< $\begin{smallmatrix} \text{O} \cdot \text{CHR} \\ \text{O} \cdot \text{CO} \end{smallmatrix}$, m.p. 187—188°, 139°, and 156°. E. W. W.

Citric acid compounds of zinc. F. S. SCHPILEV (J. Gen. Chem. Russ., 1939, 9, 1286—1293).—1 mol. of ZnSO₄ + 1 mol. of Na₃ citrate (I) give in a neutral solution Zn₂(C₆H₅O₇)₂ (II), and in an alkaline solution Na₂ZnC₆H₄O₇. An excess of (I) gives with (II) in acid solution Na₃ZnH(C₆H₅O₇)₂, in almost neutral solution Na₄Zn(C₆H₅O₇)₂, and in alkaline solution Zn(Na₃C₆H₄O₇)₂. The mechanism of the reactions is discussed. J. J. B.

Optical activity of vitamin-C.—See A., 1939, III, 1073.

Oxalate formation in ascorbic acid solutions. A. E. JURIST and W. G. CHRISTIANSEN (Amer. J. Pharm., 1939, 111, 347—350).—Solutions of Na, Ca (kept for 3 months), and monoethanolamine ascorbate are stored at 27° or 38° for ~1 year, and the H₂C₂O₄ is determined. The process is probably one of auto-oxidation (cf. Ghosh, A., 1938, II, 217). Discrepancy between loss of ascorbic acid and formation of H₂C₂O₄ is attributed to presence of other oxidation products. A. T. P.

Synthesis of *l*-ascorbic acid (vitamin-C). V. I. MAXIMOV, V. V. NIKONOVA, A. F. LAZAREV, and L. A. ZVEREVA (J. Gen. Chem. Russ., 1939, 9, 936—943).—The prep. of *l*-ascorbic acid from *l*-sorbitose has been improved to give a yield of 52—54%. Catalytic hydrogenation of *d*-glucose (+ 2% of chalk) with Raney Ni at 120—130°/8—10 atm. yields *d*-sorbitol in quant. yield. Oxidation with *Bacterium melanogenum* gives *l*-sorbitose (70% yield), from which diisopropylidene-*l*-sorbitose is obtained in 90—92% yield by treating with COMe₂, anhyd. CuSO₄, and H₂SO₄. Oxidation with KMnO₄—KOH yields 65—68% of α -ketodiisopropylidene-*l*-gulonic acid, isolated as the hydrate, from which *l*-ascorbic acid is obtained

in 76—78% yield by heating with HCl—EtOH in CHCl₃ at 60—62° for 45 hr. V. A. P.

Synthesis of uronic acids. M. STACEY (J.C.S., 1939, 1529—1531).— β -*d*-Glucose 1 : 2 : 3 : 4-tetra-acetate oxidised in AcOH with KMnO₄ in COMe₂ yields *d*-glucuronic acid tetra-acetate, which on hydrolysis with Ba(OH)₂ gives glucurone. By the same method, galactose 1 : 2 : 3 : 4-tetra-acetate yields *d*-galacturonic acid. J. D. R.

Reactivity of the mercapto-group. V. N. HELLSTRÖM (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 6, 7 pp.; cf. A., 1932, 26).—An oxidation-reduction action is observed between SH·CH₂·CO₂H and CH₂I·CO₂H, CH₂I·CO·NH₂, CHMeI·CO₂H, CO₂H·CH₂·CHI·CO₂H, and CHBr(CO₂H)₂ without solvent at 20° or in presence of H₂O at 20—25° and sometimes at 100° or in presence of C₆H₆ at 20—25° and occasionally at 60°. Such action is not observed between SH·CH₂·CO₂H and I[CH₂]₂·CO₂H, CH₂Cl(Br)·CO₂H, CH₂Cl(Br)·CO·NH₂, or CO₂H·CH₂·CHBr·CO₂H. The mode of reaction appears to be due to vicinal CO₂H, which exert a more marked effect on I than on Br. H. W.

Esters of aliphatic thio-acids of high mol. wt. A. W. RALSTON, E. W. SEGEBRECHT, and S. T. BAUER (J. Org. Chem., 1939, 4, 502—505).—The following esters have been obtained as stable compounds which can be distilled under reduced pressure without decomp. by the action of the appropriate acid chloride on the requisite mercaptan: *Me*, b.p. 112—115°/1 mm., *Et*, b.p. 115—117°/1 mm., *Pr*^a, b.p. 126—128°/1 mm., and *Bu*^a, b.p. 133—135°/1 mm., *thio-laurate*; *Me*, m.p. 34—35°, *Et*, b.p. 134—136°/1 mm., *Pr*^a, b.p. 148—150°/1 mm., and *Bu*^a, b.p. 149—151°/1 mm., *thiomyristate*; *Me*, m.p. 44—45°, *Et*, b.p. 172—175°/1 mm., *Pr*^a, m.p. 27—28°, and *Bu*^a, m.p. 29—30°, *thiopalmite*; *Me*, m.p. 50—51°, *Et*, m.p. 38—39°, *Pr*^a, m.p. 34—35.5° and *Bu*^a, m.p. 31—32°, *thioleate*; *Pr*^a *thio-oleate*, b.p. 175—178°/1 mm. H. W.

Racemisation of optically active α -alkyl- and α -phenyl-sulphonylpropionic acids.—See A., 1939, I, 618.

Kinetics of oxidation of aldehydes by selenium dioxide.—See A., 1939, I, 616.

Formation of formaldehyde by electrolysis of acetate. E. BAUR (Helv. Chim. Acta, 1939, 22, 1120—1123).—CH₂O is formed as anodic, "trivial" product during the electrolysis of solutions of AcOH; AcOH \rightarrow OH·CH₂·CO₂H \rightarrow CH₂O + CO₂. It is determined when a diaphragm is used. Without the latter there is a greater production of CH₂O owing to the change: AcOH \rightarrow AcO₂H \rightarrow CH₂O + CH₄ + O₂. The production depends on the use of d.c. and concentric Pt gauze electrodes. Formation is not observed when commutated d.c. is used and is not favoured by addition of preformed AcO₂H in Et₂O to the catholyte. Addition of EtOAc is very advantageous. The experiments support the view that the esterified CO₂H of photodynamic dyes is responsible for the CH₂O observed when they are exposed to light. H. W.

Decomposition of acetaldehyde and deuterio-acetaldehyde.—See A., 1939, I, 615.

Use of hydrogen sulphide in acetone. PÉRONNET and R. H. RÉMY (J. Pharm. Chim., 1939, [viii], 30, 170—172).—Pure COMe_2 saturated with dry H_2S forms a solution (22.4 g. per l.) stable for 6—12 months. The H_2S is not readily lost by exposure to air. After ~1 year thioketones (?) are formed in solution. J. L. D.

Transition from carbohydrates to carbocyclic compounds. I. Transformation of glucose into phenol. P. SCHORIGIN and N. N. MAKAROVA-SEMLANSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1939, 23, 915—918).—When Na is added gradually to a solution of trimethyl- β -glucosan in liquid NH_3 and the solution kept at room temp. for several days, PhOH is formed in ~20% yield. Ring-closure between $\text{C}_{(1)}$ and $\text{C}_{(6)}$ is caused by addition of Na org. compounds which are slowly formed to the bridge O and subsequent removal of O. In support of this theory it is shown that $\text{CHPh}:\text{CH}_2$ (I) is obtained in ~75% yield by the action of Na on $\text{Ph}:[\text{CH}_2]_2:\text{OH}$ (II): $(\text{II}) + \text{Na} \rightarrow \text{Ph}:[\text{CH}_2]_2:\text{ONa}$ (III) + H; $(\text{III}) \rightarrow (\text{I}) + \text{NaOH}$; $(\text{II}) + \text{NaOH} \rightleftharpoons (\text{III}) + \text{H}_2\text{O}$. H. W.

Production of reducing sugars from glycosides by ultra-violet light.—See A., 1939, I, 620.

Oxidation of aldoses by hypiodite.—See A., 1939, I, 615.

Kinetic study of the formation of *d*-glucose-phenylhydrazone.—See A., 1939, I, 616.

Biochemical synthesis of higher β -galactosides. I. VINTILESCU, C. N. IONESCU, and M. SOLOMON (Bul. Soc. Chim. România, 1938, 20, 115—125).—From determination of the solubility of galactose in mixtures of $n\text{-C}_5\text{H}_{11}\text{OH}$ and COMe_2 and polarimetric investigation of the competing reactions therein induced by emulsin, it is shown that β -*n*-amylgalactoside, m.p. 115—116°, $[\alpha]_D^{20} -9.50^\circ$ in H_2O , is best obtained in 2 : 5 $n\text{-C}_5\text{H}_{11}\text{OH}:\text{COMe}_2$. The galactoside is quantitatively hydrolysed by HCl or emulsin. R. S. C.

Structure of cellulose and other polymerides related to simple sugars. W. N. HAWORTH (Chem. and Ind., 1939, 917—925).—A lecture.

Arrangement of substituents in cellulose derivatives.—See A., 1939, I, 552.

Hydrolysis of glucosaminides by an enzyme in *Helix pomatia*. A. NEUBERGER and R. V. PITT RIVERS (Biochem. J., 1939, 33, 1580—1590).—An enzyme has been prepared from *H. pomatia* which hydrolyses only the β -forms of *N*-acetylmethylglucosaminides: it is freed from β -glucosidase by filtration through bauxite. Acyl compounds other than *N*-CHO and *N*-Ac are not hydrolysed, nor are non-acylated glucosaminides. The following have been prepared: *N*-*p*-toluenesulphonylglucosamine tetra-acetate, m.p. 128—129°, $[\alpha]_D -3^\circ$ in CHCl_3 ; 1-bromo-*N*-*p*-toluenesulphonylglucosamine triacetate, m.p. 148°, $[\alpha]_D +63.5^\circ$ in CHCl_3 ; *N*-*p*-toluenesulphonylphenylglucosaminide, m.p. 213—214°, $[\alpha]_D -83^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and its triacetate, m.p. 200—201°, $[\alpha]_D -52.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$; *N*-carbobenzyloxy- β -methylglucosaminide triacetate,

m.p. 147—149°, $[\alpha]_D +15^\circ$ in CHCl_3 ; β -methylglucosaminide formate triacetate, m.p. 120°; *N*-formyl- β -methylglucosaminide, m.p. 204—205°, $[\alpha]_D -47.2^\circ$ in H_2O , and its triacetate, m.p. 165; *N*-propionyl- β -phenylglucosaminide, m.p. 230° (decomp.), $[\alpha]_D +8^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and its triacetate, m.p. 197—197.5°; *N*-butyryl- β -phenylglucosaminide triacetate, m.p. 178—179°, $[\alpha]_D -10^\circ$ in CHCl_3 . Enzymic experiments support the theory that chitobiose, chitotriose, and chitin have a β -configuration. P. G. M.

Synthesis of α -amino-alcohols from the pyrolysis products of gas oil and the identification of some hydrocarbons contained in them. L. S. DEDUSENKO (J. Gen. Chem. Russ., 1939, 9, 1294—1302).—The light oil, b.p. 27—50° (I), obtained by the pyrolysis of gas oil at 700° was converted by addition of HOCl and distillation with KOH (or preferably NaOH, which gives a 10% better yield) into oxides in ~30% yield; of these 50% boiled at the b.p. of amylene oxides. Previous removal of a small amount of cyclopentadiene by maleic anhydride has little effect on the yield. The oxides were converted by NH_3 into α - NH_2 -alcohols from which the picrate of $\text{OH}:\text{CMe}_2:\text{CHMe}:\text{NH}_2$ (II), m.p. 134—135°, was isolated and also synthesised; this points to the presence of $\text{CMe}_2:\text{CHMe}$ in (I). (II) forms a *H* oxalate, m.p. 121—122°, and a normal oxalate, m.p. 210—210.5°, but the separation of the mixed NH_2 -alcohols through their oxalates was impracticable. α -Glycols obtained as by-products in the prep. of the oxides were dehydrated to COMePr^b and COEt_2 , showing the presence of glycols derived from $\text{CMe}_2:\text{CHMe}$ and $\text{CHMe}:\text{CHEt}$ in (I). They gave with PhNCO the urethanes of an amylene glycol, m.p. 220°, and of *cis*-cyclopentanediol, the latter derived from cyclopentene in (I). The mono- and di-urethane of $\text{OH}:\text{CMe}_2:\text{CHMe}:\text{OH}$, m.p. 125.5° and 134.4—135.5°, respectively, have been prepared.

G. A. R. K.

Amino-derivatives of pentaerythritol. II. Tetra(aminomethyl)methane. III. Di(hydroxymethyl)di(aminomethyl)methane. F. GOYAERT and M. BEYAERT (Proc. K. Akad. Wetensch. Amsterdam, 1939, 42, 637—640, 641—648; cf. A., 1934, 638).—II. $\text{C}(\text{CH}_2\text{NH}_2)_4 \cdot \text{H}_2\text{O}$, m.p. 41—42°, b.p. 108°/0.7 mm., gives a *s*-*Ac*, m.p. 60°, b.p. 72.5—73°/2 mm., and *s*-tetracarbamido-derivative, m.p. 230° (decomp.), dicarbonate, m.p. 125° (evolution of CO_2), and dimercurichloride, B_2HgCl_2 .

III. $\text{C}(\text{CH}_2\text{Br})_2(\text{CH}_2\text{OH})_2$, obtained in 50% yield with some Br_1 - and Br_2 -derivative from $\text{C}(\text{CH}_2\text{OH})_4$ by 66% HBr at 140°, is converted by NH_3EtOH (saturated at 0°) at 150° into mixed bases, whence $\text{Ac}_2\text{O}:\text{NaOAc}$ yields among other products 3 : 3-di-acetamido-1-oxacyclobutane, $\text{O} < \text{CH}_2 > \text{C}(\text{CH}_2\text{NHAc})_2$, m.p. 79°, b.p. 79—80°/0.1 mm., which with boiling 48% HBr gives β -bromomethyl- β -hydroxymethylpropylene- α - γ -diamine dihydrobromide, m.p. 246° (decomp.). $\text{Cl}(\text{CH}_2)_2\text{O}]_2$ (modified prep.) is converted by H_2O at 150—160° quantitatively into $\text{C}(\text{CH}_2\text{OH})_4$, is unaffected by liquid NH_3 at 100° but decomposed at 200°, and with aq. NH_3 (saturated at 0°) at 190° gives 78% of $\beta\beta$ -di(hydroxymethyl)propylene- α - γ -diamine,

+H₂O, cryst., b.p. ~200°/0.002 mm. [H₂ oxalate, m.p. 168° (decomp.); dipicrate, m.p. 223° (decomp.); carbonate at 164° gives CO₂ and the diamine hydrate].

R. S. C.

Syntheses of basic amino-acids and glycine. D. W. ADAMSON (J.C.S., 1939, 1564—1568).—Slow addition of HN₃ in CHCl₃ to *d*-glutamic acid in H₂SO₄-CHCl₃, followed by pptn. with phosphotungstic acid and decomp. of the phosphotungstate with Ba(OH)₂, gives *d*-α-diamino-*n*-butyric acid (isolated as oxalate) (dipicrate, m.p. 180—181°). NaN₃ may be used in place of HN₃, and after decomp. of the phosphotungstate with Ba(OH)₂, the NH₂-acid may be isolated, via the picrate, as the *dihydrochloride*, m.p. 195—196° (decomp.). Similarly, α-aminopimelic acid (I) in CHCl₃-H₂SO₄ treated with HN₃ in CHCl₃ or with NaN₃ yields *dl*-lysine (II) (isolated as monopicrate or dihydrochloride via the phosphotungstate) (dipicrate, m.p. 188—190°). Et cyclohexanone-2-carboxylate and HN₃ in C₆H₆, on treatment with HCl (gas) yields impure (I), and (II). The reaction also succeeds in CHCl₃ using HCl (gas) or conc. aq. HCl. α-Aminoadipic acid in H₂SO₄, when treated with HN₃ in CHCl₃, yields *dl*-ornithine (III) [sulphate, m.p. 223° (decomp.) (lit. 213° to 234°)]. Et cyclopentanone-2-carboxylate and HN₃ in CHCl₃, treated with HCl, also yields (III). Treatment of CH₂(CO₂H)₂ in H₂SO₄ with HN₃ in CHCl₃ yields glycine.

J. D. R.

Poly-condensation of α-amino-acid esters. M. FRANKEL and E. KATCHALSKI (Nature, 1939, 144, 330—331).—Solutions of NH₂·CH₂·CO₂Et (I) in solvents such as C₆H₆ or xylene on keeping at room temp. or at the b.p. deposit horn-like products insol. in H₂O and containing polypeptide esters of different chain lengths. (I) gradually solidifies, and after keeping for several weeks hexadecaglycine Et ester was isolated from the O₂-treated ester and eikosi-glycine Et ester from that treated with H₂. Under suitable conditions NH₂·CHMe·CO₂Et yields, *inter alia*, condensation products which give a strong biuret reaction and appear to be alanine polypeptide esters.

L. S. T.

Condensation of the hexapeptide ester of glycine into the 96- and higher (3 × 2ⁿ) peptide esters. E. PACSV (Nature, 1939, 144, 551).—At 102°±1°, the hexapeptide ester undergoes the type of condensation characteristic of the tripeptide ester yielding, in a series of successive bimol. reactions, the 12-, 24-, 48-, 96- (3 × 2ⁿ) peptide esters. With *n* > 4 the average rate of the reaction, with 1 hr. as the time unit, is *k* = 150 × 10⁻⁴. The activation energy is ~38 kg.-cal. Neither "cyclol 6" nor nonapeptide ester is formed during the reaction. The esters obtained are colourless, amorphous substances, slightly sol. in cold H₂O, insol. in EtOH, sol. in conc. HCl and in conc. aq. CO(NH₂)₂; the biuret reaction is strong.

L. S. T.

Configuration of glutamic and aspartic acids from pathogenic bacteria.—See A., 1939, III, 1015.

Combination of cysteine with sugars. M. P. SCHUBERT (J. Biol. Chem., 1939, 130, 601—603; cf. A., 1936, 824).—Cysteine hydrochloride and the sugar are shaken with H₂O and the solution is kept H H* (A., II.)

for 48 hr. at room temp., after which C₅H₅N is added after an additional period of 50—70 hr., and then abs. EtOH is introduced. Cysteine (I) thus give compounds, C₈H₁₅O₆NS, with *d*-arabinose (Zn salt) and *d*-xylose, m.p. 153° and 133° respectively, substances, C₉H₁₇O₇NS, with *d*-glucose (II), *d*-mannose (acetate, m.p. 150—152°), and *d*-galactose (III), m.p. 167°, 171°, and 138°, and compound, C₁₅H₂₇O₁₂NS, m.p. 130°, with lactose (IV). Fructose does not form a compound with (I). The properties of these compounds are similar to those of the thiazolidines formed by condensation of (I) with simple aldehydes. Their solutions are acid to litmus. In solutions containing an excess of NaHCO₃ none of these compounds gives a positive SH test with Na nitroprusside (V). In a dil. solution of NH₃ and (NH₄)₂SO₄ only the compounds formed from (II) and (IV) give fair tests with (V); the remainder give only very faint reactions. Aq. solutions of all these compounds absorb I as rapidly as does free (I) and in amount equiv. to the (I) which they contain; such solutions which have been titrated with I slowly deposit crystals of cystine. In solutions containing NaHCO₃ in which a negative test with (V) is given, these compounds rapidly yield *S*-carboxymethylcysteine with CH₃I·CO₂Na. In glacial AcOH (III) gives gelatinous *galactose-2 : 4-dinitrophenylhydrazone*, m.p. 171—173°; under these conditions the compound from (I) and (III) remains unaffected. (III) does not appear to unite with SH·CH₂·CO·NH₂ or SH·CPh₂·CO₂H. H. W.

Reaction of α-thiocyanopropionic acid with water.—See A., 1939, I, 617.

Reduction of certain amides and substituted amides. I. Electro-reduction of cyclopeptide and open peptide groups. N. I. GAVRILOV and A. V. KOPERINA (J. Gen. Chem. Russ., 1939, 9, 1394—1401).—The CO group of amides of aromatic acids readily undergoes electro-reduction. For the amides R·CO·NHR' or R·CO·NR'₂ reduction is possible when R = H or Me and R' = Me or Ph, but not when R contains >1 C. The CO group of peptides does not, but those of diketopiperazine do, undergo reduction at a Pb cathode.

R. T.

Silico-organic compounds. I. Preparation of silicon analogues of aliphatic ortho-esters. H. W. POST and C. H. HOFRICHTER, jun. (J. Org. Chem., 1939, 4, 363—364).—The esters are prepared by heating Si(OEt)₄ with a Grignard reagent and treating the product with an aliphatic alcohol, e.g., Si(OEt)₄ + MgEtBr → MgBr·OEt + SiEt(OEt)₃ (I) and (I) + 3PrⁿOH ⇌ 3EtOH + SiEt(OPrⁿ)₃. In an individual case SiCl₄ is treated with a Grignard reagent followed by PrⁿOH. The following are described: Et₃, b.p. 158—160°, Pr₃, b.p. 202—204°/760 mm., Bu₃, b.p. 235—238°/760 mm., tri-*n*-, b.p. 285°/760 mm. and -iso-*amyl*, b.p. 266—269°/760 mm., orthosilicopropionate, Et₃ orthosilicobutyrate, b.p. 179—180°/760 mm.; Et₃, b.p. 235—238°/760 mm., and Pr₃, b.p. 192°/7 mm., orthosilicobenzoate, *n*-heptyl orthosilicate, b.p. 213.5°/4 mm.

H. W.

Organic reineckates. M. COUPECHOUX (J. Pharm. Chim., 1939, [viii], 30, 118—129).—Limiting concns., the Cr and CNS contents, and the solubilities

in H_2O and MeOH at room temp. and in EtOH at 96° of the reineckates of 45 org. bases, prepared by adding a solution of the base in 5% HCl to excess of $[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]\text{NH}_4\cdot\text{H}_2\text{O}$, are recorded. Now *reineckates* are those of betaine (I), β -methylcholine, bromocholine, neurine, $\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3$ (II), $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, *o*- and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ (III), 1 : 2 : 5- $\text{C}_6\text{H}_4\text{Me}(\text{NH}_2)_2$, benzidine, hydroxyquinoline, $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, brucine, stovaine, cocaine, and ephedrine. The small amounts of CNS' left in solution can be determined by the method described previously (A., 1936, 1219). Most of the reineckates are micro-cryst.; (I) forms lance-shaped plates; (II), small hexagonal plates; and (III), fern-like leaflets. The reineckates are anhyd., stable at room temp., slowly hydrolysed by cold and rapidly by hot H_2O . In general, the formula is $[\text{Cr}(\text{NH}_3)_2(\text{CNS})_4]_2\text{base}^+$; the reineckates of antipyrine, pyrimidone, and quinine are not well-defined. All are sol. in COMe_2 . Factors affecting solubility are discussed. L. S. T.

New class of ammines. Complex thiostannates.—See A., 1939, I, 622.

New complex ammines belonging to the group of iron and cobalt dinitrosothiosulphates.—See A., 1939, I, 623.

Constitution of complex metallic salts. X. Further evidence for the structure of bridged dipalladium derivatives. J. CHATT and F. G. MANN (J.C.S., 1939, 1622—1634).—*n*- $\text{C}_8\text{H}_{17}\cdot\text{SH}$ with CH_2Br_2 and NaOEt gives *ethylene- $\alpha\beta$ -bis-(*n*-octyl sulphide)*, m.p. 29° , which with $(\text{NH}_4)_2\text{PdCl}_4$ (I) yields *ethylene- $\alpha\beta$ -bis-(*n*-octyl sulphide)dichloropalladium* (II), darkens $\sim 270^\circ$, m.p. $\sim 280^\circ$. *o*-Phenylenebis(dimethylarsine) in EtOH with (I) gives *di-o-phenylenebis(dimethylarsine)palladium dichloride*, which with (I) in HCl-EtOH gives *di-o-phenylenebis(dimethylarsine)palladium palladochloride* and *o-phenylenebis(dimethylarsine)dichloropalladium* (III). *o*-Phenylenebis(*di-n*-butylarsine) similarly gives *di-o-phenylenebis(di-n-butylarsine)-palladium dichloride tetrahydrate* and *dichloropalladium* (IV), m.p. $273\text{—}275^\circ$. AsPhCl_2 with the Grignard reagent from Bu^aBr gives *phenyldi-n-butylarsine*, b.p. $158\text{—}161^\circ/21\text{ mm.}$, which with (I) gives *bis(phenyldi-n-butylarsine)dichloropalladium*, m.p. 47° , which when boiled with (I) in EtOH or COMe_2 yields *dichlorobis(phenyldi-n-butylarsine)- μ -dichlorodipalladium*, m.p. 166° . PPh_3 with (I) in EtOH gives *bis(triphenylphosphine)dichloropalladium*, decomp. $\sim 250\text{—}270^\circ$, which with (I) in EtOH and CHCl_3 yields *dichlorobis(triphenylphosphine)- μ -dichlorodipalladium* (V). *Ethylene- $\alpha\beta$ -bis(diphenylarsine)* with (I) yields *ethylene- $\alpha\beta$ -bis(diphenylarsine)dichloropalladium* (VI), decomp. at high temp. The BuPh (VII), α -form, m.p. $172\text{—}174^\circ$, and β -form, m.p. $185\text{—}186^\circ$, derivative was prepared similarly. AsBu_2Cl with NaOH and $\text{C}_2\text{H}_5\text{Br}_2$ yields *ethylene- $\alpha\beta$ -bis(arsinic acid)*, m.p. $201\text{—}202^\circ$ (decomp.), which in dil. HCl with aq. KI gives *ethylene- $\alpha\beta$ -bis(butylchloroarsine)*, b.p. $160\text{—}165^\circ/0.05\text{ mm.}$, and this with the Grignard reagent from Bu^aBr under H_2 provides *ethylene- $\alpha\beta$ -bis(dibutylarsine)*, b.p. $161\text{—}162^\circ/0.04\text{ mm.}$, which with (I) yields *ethylene- $\alpha\beta$ -bis(dibutylarsine)dichloropalladium* (VIII), m.p. 221° . All attempts to bridge (II), (III), (IV), (V), (VI), (VII),

and (VIII) with (I) were unsuccessful. *Dichlorobis(tributylarsine)- μ -dichlorodipalladium* (IX) in Et_2O with NH_3 (2 mols.) in EtOH gives *dichloromononaminotributylarsinepalladium*, m.p. $73\text{—}74^\circ$ (decomp.), which in cold *cyclohexane* deposits (IX). AsBu_3 with $\text{K}_2\text{Pd}(\text{NO}_2)_4$ yields $(\text{Bu}_3\text{As})_2\text{Pd}(\text{NO}_2)_2$ but with $\text{K}_2\text{Pd}(\text{SCN})_4$ gives both $(\text{Bu}_3\text{As})_2\text{Pd}(\text{SCN})_2$ and $(\text{Bu}_3\text{As})_2\text{Pd}_2(\text{SCN})_4$. It is concluded that reactions previously described (A., 1936, 1184, 1496) do not support an unsymmetrical structure for bridged dipalladium derivatives, the tautomerism deduced from the dipole moments being attributed to the *cis* and *trans* symmetrical forms. F. R. G.

Kinetics of vapour-phase reaction of cyclopropane with iodine.—See A., 1939, I, 615.

Isomerisation of polymethylene hydrocarbons with aluminium chloride. M. B. TUROVA-POLLAK and Z. MAKAEVA (J. Gen. Chem. Russ., 1939, 9, 1279—1282).—When heated with AlCl_3 for 20 hr. at $110\text{—}115^\circ$ *ethylcyclopentane* (I) is isomerised to the extent of 97% into *methylcyclohexane* (II), recognised by dehydrogenation with Pt-asbestos at $300\text{—}310^\circ$ to PhMe . (II) with AlCl_3 only gives 6.3% of (I). G. A. R. K.

Synthesis of *tert*-butyl- and *tert*-amyl-cyclopentane and of intermediate products. H. PINES and V. N. IPATIEV (J. Amer. Chem. Soc., 1939, 61, 2728—2730).— $\text{H}_2\text{-Ni}$ at $125^\circ/100\text{ atm.}$ converts *p*- $\text{C}_6\text{H}_4\text{Bu}^t\cdot\text{OH}$ and *p-tert*-amylphenol into *4-tert*-butyl-, m.p. 82° , and *4-tert*-amyl-cyclohexanol, m.p. $24\text{—}25^\circ$, b.p. $154\text{—}155^\circ/40\text{ mm.}$ (α -naphthylurethane, m.p. 113°), oxidised by 50% HNO_3 in presence of a little NH_4 vanadate to β -*tert*-butyl-, m.p. 117° , and β -*tert*-amyl-adipic acid, m.p. $77\text{—}78^\circ$, which with $\text{Ba}(\text{OH})_2$ at 280° give *3-tert*-butyl-, b.p. $200\text{—}201^\circ/759\text{ mm.}$ [*semicarbazone*, m.p. $194\text{—}194.5^\circ$ (decomp.); *2 : 4-dinitrophenylhydrazones*, m.p. 139°], and *3-tert*-amyl-cyclopentanone, b.p. $120^\circ/27\text{ mm.}$ (*semicarbazone*, m.p. 189° ; *2 : 4-dinitrophenylhydrazones*, m.p. $174\text{—}5^\circ$), respectively. $\text{H}_2\text{-Ni}$ at $80^\circ/100\text{—}60\text{ atm.}$ then gives *3-tert*-butyl-, b.p. $196\text{—}198^\circ/744\text{ mm.}$ (α -naphthylurethane, m.p. 95°), and *3-tert*-amyl-cyclopentanol, b.p. $217^\circ/738\text{ mm.}$ (α -naphthylurethane, m.p. 82°), dehydrated by activated Al_2O_3 at 345° to *3*- or *4-tert*-butyl-, b.p. $139\text{—}6^\circ/760\text{ mm.}$, and *tert*-amyl- Δ^1 -cyclopentene, b.p. $163\text{—}165^\circ/743\text{ mm.}$, hydrogenated (Ni ; $60^\circ/100\text{ atm.}$) to *tert*-butyl-, m.p. $-96^\circ\pm 0.2^\circ$, b.p. $145\text{—}2^\circ/760\text{ mm.}$, and *tert*-amyl-cyclopentane, b.p. $173\text{—}9^\circ/760\text{ mm.}$, respectively. Physical consts. of the products are given. R. S. C.

Hydrogenation catalysis of phenylcyclopentane and its homologues. J. I. DENISENKO (J. Gen. Chem. Russ., 1939, 9, 1068—1076).—*Phenylcyclopentane* is hydrogenated (Pt-C catalyst at 300°) to a mixture of α -, β -, and γ -phenylpentane, showing that rupture of the cyclopentane ring takes place in all three possible positions. The same applies to cyclopentylphenyl-methane, -ethane, -propane, -butane, and -pentane, which yield mixtures of isomeric hexyl-, heptyl-, octyl-, nonyl-, and decyl-benzene, respectively. R. T.

Contact isomerisation of ϵ -cyclohexyl- Δ^a -pentene and ϵ -cyclohexyl- Δ^a -pentinene. P. J. LEVINA, G. B. GOLUB, and K. M. SMIRNOV (J. Gen.

Chem. Russ., 1939, 9, 825—828).—A mixture of amylbenzene and amylcyclohexane in the proportions of 1 : 2 and 2 : 1, respectively, is formed from ϵ -cyclohexyl- Δ^a -pentene and from ϵ -cyclohexyl- Δ^a -pentinene, by passage over Pt-C at 200—205°. V. A. P.

Directive influence of the electric moment on substitution in the benzene ring.—See A., 1939, I, 551.

Electronic interpretation of the halogenation of toluene. A. P. KRESCHKOV (J. Gen. Chem. Russ., 1939, 9, 1251—1257).—Theoretical. The author introduces the term "electronisation" to denote the electron density surrounding a given atom, which is affected both by structure and external conditions, and explains the behaviour of PhMe in terms of this. Side-chain halogenation is due to tautomerism which includes as one of the limiting phases one with a semicyclic double linking (Schorigin); this form is favoured by external activation. G. A. R. K.

Ozonisation of *o*-xylene and the structure of the benzene ring. J. P. WIRAUT and P. W. HAAYMAN (Nature, 1939, 144, 290).—Ozonisation of *o*-xylene (I) in CHCl_3 at -25° and conversion of the decomp. products of the ozonides into oximes [20% yield on (I)] gave dimethylglyoxime (0.88 mol.), methylglyoxime (2 mols.), and glyoxime (3.2 mols.). This supports the qual. results of Levine *et al.* (A., 1932, 259), and affords chemical evidence for the occurrence of two resonating Kékulé structures in (I).

L. S. T.

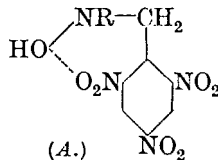
Mechanism of aromatisation. Thermal isomerisation of the xylenes. A. F. DOBRIANSKI and F. J. SAPRIKIN (J. Gen. Chem. Russ., 1939, 9, 1313—1314).—Pyrolysis of *o*- (I), *m*- (II), and *p*- (III)-xylene in a porcelain tube heated in an electric oven at 700—770° gives in each case PhMe, condensation products, gases, and unchanged xylene. The recovery of (II) was the highest and it appears to be the most stable, (I) the least stable and the most easily demethylated. Some isomerisation of (I) into (II) and (III) and of (III) into (II), but not into (I), is also observed; (II) is not isomerised. It is probable that demethylation and isomerisation proceed concurrently and that (II) is not an intermediate in the formation of PhMe. G. A. R. K.

Relative reactivity of chloro- and bromo-nitrobenzenes. N. N. VOROSHOV, jun., and V. A. KOBELEV (J. Gen. Chem. Russ., 1939, 9, 1047—1048).— Na_2SO_3 does not react with *o*-, *m*-, or *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ or $\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ under the conditions of Sprung's experiments (A., 1930, 759). The alleged reactivity of halogens in the *m*-position is thus not confirmed.

R. T.

Properties of nitro-groups. Trinitrobenzene derivatives. D. RĂDULESCU, L. NOVAC, I. PETREANU, and S. POPA (Bul. Soc. Chim. România, 1938, 20, 49—88).—An electronic interpretation of the structure of additive compounds of $\text{C}_6\text{H}_3(\text{NO}_2)_3$ etc. is given; formation of such complexes loosens substituents such as CO_2H , CHO , and NO_2 , and even H (reaction with BzCl in absence of AlCl_3). 1 : 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ with NO-compounds gives products (A), in which $\text{R} = p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$ (cf.

Secăreanu, A., 1931, 752), *Ph*, m.p. 146—149° (explosive), *p*-, m.p. 151—153° (explosive), *m*-, m.p. 155—157° (explosive), and *o*- $\text{C}_6\text{H}_4\text{Me}$, m.p. 147—149° (explosive), and *p*- $\text{C}_6\text{H}_4\cdot\text{NPh}_2$ (I), m.p. 221—223° (decomp.), which lose NO_2 when heated alone or in neutral solvents [in COMe_2 or CHCl_3 for (I)] and give only small amounts of the amine and $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{CHO}$ (II) when hydrolysed. 2 : 4 : 6-Trinitro-



benzylidene-*p*-, m.p. 201—202° (decomp.), *m*-, m.p. 193—194° (decomp.), and *o*-toluidine, m.p. 197—198° (decomp.), and di-2 : 4 : 6-trinitrobenzylidene-*p*-phenylenediamine, m.p. 208° (explosive), are prepared from (II) and the appropriate amine, are readily hydrolysed to the components, and do not lose NO_2 when heated. In accordance with electronic considerations, *o*-, *m*-, and *p*- $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, *p*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$, $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{Hal}$, and $\text{C}_6\text{HMe}_2(\text{NO}_2)_3$ do not give compounds of type (A), but failure by $\text{C}_6\text{H}_2\text{Et}(\text{NO}_2)_3$ is inexplicable. 5 : 1 : 2- $\text{NO}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{CO}_2\text{Me}$ and $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$ give a compound which is neither a Schiff's base nor of type (A). 2 : 4 : 6 : 1 : 3- $(\text{NO}_2)_3\text{C}_6\text{H}(\text{CO}_2\text{H})_2$ (III), m.p. 204—206°, is best obtained by adding solid KMnO_4 to 1 : 3 : 2 : 4 : 6- $\text{C}_6\text{HMe}_2(\text{NO}_2)_3$ in oleum (*d* 1.87); it loses 2 CO_2 when heated in H_2O . Trinitrotrimesic acid (IV), m.p. $\sim 208^\circ$ (decomp.) (Ag salt), is similarly obtained in presence of 0.5—0.7% of fuming HNO_3 as catalyst from 2 : 4 : 6 : 1 : 3 : 5- $\text{C}_6\text{Me}_3(\text{NO}_2)_3$. (III) and (IV) are very sol. in H_2O , EtOH , etc., insol. in hydrocarbons, give sol. salts, are fully ionised (all CO_2H in 0.0001M. aq. solution, and, as also is $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{CO}_2\text{H}$, are determined by their nitron salts (1 mol. of nitron per CO_2H). *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ (V) and saturated aq. $\text{Ba}(\text{OH})_2$ at 40° in absence of air give a red salt, $[\text{C}_6\text{H}_3(\text{NO}_2\cdot\text{OH})_3]_2\text{Ba}_3\cdot 12\text{H}_2\text{O}$, which with HCl regenerates (V) and over H_2SO_4 at room temp. in vac. gives the reddish-brown "salt," $\text{C}_6\text{O}_6\text{N}_3\text{Ba}_{1.5}\cdot 3\text{H}_2\text{O}$; further drying at 140° over P_2O_5 in vac. then gives the "salt," $\text{C}_6(\text{NO}_2)_3\text{Ba}_{1.5}$, unusually stable to acid and converted thereby into a brown insol., micro-cryst. substance, $[\text{C}_6\text{H}_3(\text{NO}_2)_3]_2$. The Ba in the last-mentioned "salt" is considered to be attached to the nuclear C. $\text{Sr}(\text{OH})_2$ gives an unstable, hydrated salt, converted by drying at 110° into an explosive, reddish-brown "salt," $[\text{C}_6(\text{NO}_2)_3]_2\text{Sr}_3$. TiOH gives only a reddish-violet, hydrated Ti_1 salt, converted over H_2SO_4 at room temp. into a substance, $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{TiOH}$. Guanidine gives a red salt, $[\text{C}_6\text{H}_3(\text{NO}_2)_3]_2(\text{CH}_5\text{N}_3)_3\cdot\text{H}_2\text{O}$. 2 : 4 : 6 : 1- $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{CO}_2\text{H}$ and $\text{Ba}(\text{OH})_2$ give first the normal, colourless $\text{Ba}_{0.5}$ salt and then a red "salt," $(\text{NO}_2)_3\text{C}_6\text{Ba}\cdot\text{CO}_2\text{Ba}_{0.5}\cdot\text{Ba}_{0.5}\text{OH}\cdot 3\text{H}_2\text{O}$, dehydrated at 114° to the anhyd. "salt"; "salts," $\text{C}_7\text{H}_3\text{O}_8\text{N}_3\text{Sr}_2\cdot 2.5\text{H}_2\text{O}$ and anhyd., are similarly obtained. (III) gives a salt, $[\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{CO}_2]_2\text{Ba}_5(\text{OH})_6\cdot\text{H}_2\text{O}$, dehydrated in vac. and reconverted by HCl into (III). (IV) and BaCO_3 give a colourless $\text{Ba}_{1.5}$ salt, $+12\text{H}_2\text{O}$ and anhyd., converted by $\text{Ba}(\text{OH})_2$ into a "salt," $[\text{C}_6(\text{NO}_2)_3(\text{CO}_2)_3](\text{BaOH})_3\cdot 6\text{H}_2\text{O}$ and anhyd., reconverted into (IV) by HCl . $[\text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ and $\text{Ba}(\text{OH})_2$ give, with loss of NO_2 , an impure product,

$C_{12}H_4(NO_2)_6[Ba(OH)_2]_3$, which at 114° loses $\sim 4H_2O$. 1 : 2 : 4 : 6 : $C_6H_2Me(NO_2)_3$ gives a mixture, $C_6H_2Me(NO_2)_3[Ba(OH)_2]_n$, in which n is partly 2 and partly 3. $C_6HMe_2(NO_2)_3$ gives a coloured solution, but no solid salt, and $C_6Me_3(NO_2)_3$ does not give even a colour. 2 : 4 : 6 : $(NO_2)_3C_6H_2 \cdot OH$ gives a product, $C_6H_2(NO_2)_3 \cdot OH \cdot (BaOH)_2 + 0.5H_2O$, which at $107-110^\circ/\text{vac.}$ loses H_2O . 2 : 4 : 6 : 1 : 3 : $(NO_2)_3C_6H(OH)_2$ gives a substance, $[(NO_2)_3C_6HO_2]Ba_3(OH)_2 + 2H_2O$. Trinitro-orsinol gives only the Ba_1 salt, $+2H_2O$. n are recorded for some polynitro-compounds. R. S. C.

Synthesis of sulphonyl chlorides by chlorination of sulphur compounds. T. B. JOHNSON (Proc. Nat. Acad. Sci., 1939, 25, 448—452).—The production of RSO_2Cl by the action of Cl_2-H_2O on $SR \cdot C \begin{smallmatrix} N: CX \\ N: CH \end{smallmatrix} > CH$ (I), $SR \cdot C(NR') \cdot NR'_2$ (e.g., $R' = H$ or Me), and $RSCN$ (cf. Johnson *et al.*, lit. 1935—1939) is considered to involve preliminary formation of the sulphoxide (A) and then $RSOCl$; (A) may undergo oxidation (to the sulphone) or hydrolysis (to RSO_2H or $RSOCl$). $SR \cdot C \begin{smallmatrix} NH \cdot CO \\ N: CH \end{smallmatrix} > CH$ can be differentiated from (I) since these give $CO \begin{smallmatrix} NH \text{---} CO \\ NH \cdot CH(OH) \end{smallmatrix} > CCl_2$ and RSO_3H .

Preparation of styrenes by the action of organomagnesium compounds on *p*-cyclohexylacetophenone. I. ZUGRAVEȘCU and (MME.) S. ZUGRAVEȘCU (Bul. Soc. Chim. România, 1938, 20, 225—230).—*p*-cyclohexylacetophenone and the appropriate Mg alkyl bromide give β -*p*-cyclohexyl- Δ^2 -*n*-butene, b.p. $169^\circ/4$ mm., *n*-pentene, b.p. $157-158^\circ/12$ mm., and *n*-hexene, b.p. $191-192^\circ/15$ mm. $MgPhBr$ gives α -*p*-cyclohexylphenylstyrene, b.p. $223-224^\circ/13$ mm. The structure of the products is proved by $KMnO_4$ -oxidation. R. S. C.

Ease of polymerisation of substituted styrenes in relation to their structure. II. P. P. SCHORIGIN and N. V. SCHORIGINA (J. Gen. Chem. Russ., 1939, 9, 845—854).—Polymerisation at 100° and at 170° in absence of catalysts has been studied in the cases of styrene, *o*- and *p*-bromo-, *o*- and *p*-methoxy-, and *o*- and *p*-amino-styrene, Δ^2 -octene, cyclohexylethylene, anethole, safrole, isosafrole, eugenol, isoeugenol, $CHPh:CHMe$, $CPhMe:CH_2$, $CPh_2:CH_2$, and $CHPh:CHBr$. It is concluded that in substituted ethylenes, polymerisation takes place only when the double linking is conjugated with an aromatic nucleus. Polymerisation of the styrenes is retarded by substitution at α and β and by increase of mol. wt. Rise in temp. leads to increase in velocity of polymerisation, but to decrease in chain length of the polymeride. The following are described: β -*p*-diphenyllethyl alcohol, m.p. $93-94^\circ$, from $(CH_2)_2O$ and *p*- $C_6H_4Ph \cdot MgI$; α -*p*-, b.p. $145^\circ/20$ mm., and α -*o*-bromophenylethyl alcohol, b.p. $128^\circ/15$ mm., from *p*- and *o*- $C_6H_4Br \cdot CHO$ and $MeMgI$. Dehydration of the ethanols with $KHSO_4$ at $130-140^\circ$ gives *p*- and *o*-bromostyrene, b.p. $102-104^\circ/20$ mm. and $102-104^\circ/22$ mm., respectively. V. A. P.

Effect of substitution on the dissociation of hexa-arylethanes. VIII. Disproportionation of tri-*p*-tolylmethyl. C. S. MARVEL, W. H. RIEGER, and M. B. MUELLER. IX. Disproportionation of hexa-*p*-alkylphenylethanes. Effect of *o*-, *m*-, and *p*-alkyl groups on the dissociation of hexa-arylethanes. C. S. MARVEL, M. B. MUELLER, C. M. HIMEL, and J. F. KAPLAN (J. Amer. Chem. Soc., 1939, 61, 2769—2771, 2771—2775; cf. A., 1939, II, 498).—VIII. It is shown by χ (extrapolated to zero time) that, when pure $(p-C_6H_4Me)_3CCl$ (I) is shaken with Ag in C_6H_6 , 20% of $(p-C_6H_4Me)_3C$ (II) is present in 0.05M. solution. After a few hr. at $25-30^\circ$, the orange colour has completely disappeared and χ shows absence of (II). This is due to disproportionation of (II) to $(p-C_6H_4Me)_3CH$ (which is recovered by distillation at $\sim 85^\circ/10^{-4}$ mm.) and $(p-C_6H_4Me)_2C:C_6H_4:CH_2$, which polymerises to a colourless glass. A similar glass is obtained from (I) by C_5H_5N in absence of O_2 .

IX. It is shown by χ that $(p-C_6H_4R)_3C$ ($R = Et$, Pr^a , Pr^b , $CHMeEt$, or Bu^b), when kept at 30° , disproportionate into $(p-C_6H_4R)_3CH$ and $(p-C_6H_4R)_2C:C_6H_4:CHR'$ (A). However, decolorisation does not occur, since (A) are coloured and do not polymerise. The relative rates of disproportionation decrease in the order of R given above. Initial degrees of dissociation (extrapolated to zero time) are $R = Et$ 17, Pr^a 21, Pr^b 26, $CHMeEt$ 33, and Bu^b 27% (all $\pm 2\%$). This interpretation of the results is supported by the fact that $(m-C_6H_4Me)_3C$, which exists $\pm 40\%$ as free radical and cannot yield a quinonoid disproportionation product, is quite stable in C_6H_6 . *o*- $C_6H_4Me \cdot CPh_2Cl$ gives an ethane, dissociated to 25 (± 1)% to a stable radical; the stability and high degree of dissociation are probably due to steric reasons. $(p-C_6H_4Bu^a \cdot CPh_2)$ dissociates to 8—9 (± 1)% to a radical, which is stable as it cannot give a quinonoid product, but $(p-C_6H_4Me \cdot CPh_2)_2$ and $(p-C_6H_4Pr^b \cdot CPh_2)_2$ dissociate to 5 and 8—10 (± 1)%, respectively, to radicals which disproportionate, but more slowly than does $(p-C_6H_4R)_3C$. The following data are incidentally recorded. Diphenyl-*p*-isopropyl-, m.p. $90-91^\circ$, and *p*-tert.-butylphenylmethyl chloride, m.p. $133-134^\circ$; diphenyl-*o*-tolyl-, m.p. $148-149^\circ$, *p*-isopropylphenyl-, m.p. $139-140^\circ$, and *p*-tert.-butylphenyl-methyl peroxide, m.p. $156-157^\circ$. R. S. C.

Cracking of decalin under pressure.—See A., 1939, I, 615.

Conversion of 1- into 2-bromonaphthalene. H. E. FISHER and R. H. CLARK (Canad. J. Res., 1939, 17, B, 251—252).—Conversion of 1- into 2- $C_{10}H_7Br$ (I) by $AlCl_3-CS_2$ (method: Roux, A., 1886, 806) gives a max. yield of 9.1%. Addition of Ni, Mo, W, Sb, Se, or Cr increases the yield of (I) to 25.5, 25.0, 23.5, 22.5, 16, or 14.4%, respectively. Replacement of CS_2 by $COMe_2$, C_6H_6 , $EtOH$, aq. $EtOH$, dioxan, aq. or anhyd. C_5H_5N , or $MeNO_2$, or of $AlCl_3$ by $FeCl_3$, gave no conversion. A. T. P.

Dehydrogenation. IV. [Tetrahydronaphthalenespirocyclopentanes.] S. C. SEN-GUPTA (J. Indian Chem. Soc., 1939, 16, 349—356).—The anhydride (I) of 1-carboxycyclopentane-1-acetic acid in

PhMe with AlCl_3 gives 1-*p*-tolacylcyclopentane-1-carboxylic acid (II), m.p. 149–150° (semicarbazone, m.p. 164–165°), the *Me* ester, b.p. 170–175°/5 mm., of which is obtained from *Me* cyclopentane-1-acetate-1-carboxyl chloride (III), PhMe, and AlCl_3 [during which reaction a rearrangement of (III) is assumed]. Zn–Hg in conc. HCl reduces (II) to 1- β -*p*-tolylethylcyclopentane-1-carboxylic acid, m.p. 68–69°, b.p. 186–190°/5 mm. (anilide, m.p. 124°; *Et* ester, b.p. 160–162°/5 mm.), converted by 85% H_2SO_4 into the 1-*keto*-derivative, b.p. 160–163°/5 mm. (semicarbazone, m.p. 141–142°), of 7-methyl-1:2:3:4-tetrahydronaphthalene-2:2-spirocyclopentane (IV), b.p. 135–136°/6 mm., to which it is reduced by Zn–Hg in conc. HCl. Se dehydrogenation of (IV) at 340–350° gives 3-methylphenanthrene and 2-methylanthracene (?). With PhEt and AlCl_3 in CS_2 , (I) and (III) give respectively 1-*p*-ethylphenacylcyclopentane-1-carboxylic acid (V), m.p. 128–129° (semicarbazone, m.p. 130°), and its *Me* ester, b.p. 195–198°/10 mm. (V) is reduced to 1- β -*p*-ethylphenylethylcyclopentane-1-carboxylic acid, m.p. 51–53°, b.p. 200–202°/9 mm. (anilide, m.p. 117°; *Et* ester, b.p. 144–146°/5 mm.). This gives the 1-*keto*-derivative, b.p. 175°/9 mm., of 7-ethyl-1:2:3:4-tetrahydronaphthalene-2:2-spirocyclopentane, b.p. 154–156°/9 mm., dehydrogenated to 3-ethylphenanthrene and 2-ethylanthracene (?). The mechanism proposed by Linstead (Ann. Rep. Chem. Soc., 1936, 33, 304) for dehydrogenations of this type (cf. A., 1934, 1003) is rejected in favour of 1:2-fission of the cyclopentane ring during dehydrogenation. E. W. W.

Halogen derivatives of acenaphthene. M. M. DASCHEVSKI and A. P. KARISCHIN (Prom. Org. Chim., 1939, 6, 507–511).—Acenaphthene and SO_2Cl_2 in presence of I at room temp. give 3:4-dichloroacenaphthene (I), in 50–60% yield. (I) and H_2SO_4 (1 hr. at 100°) give 3:4-dichloroacenaphthene-1-sulphonic acid, m.p. 192° (decomp.) [chloride, m.p. 179°; amide, m.p. 270–272° (decomp.)], oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$) to 4:5-dichloro-2-sulphonaphthalic acid, m.p. 229–230° (anhydride, m.p. 160°; chloride, m.p. 219–220°; amide, decomp. 380–382°). 3:4-Dichloroacenaphthene-1:6-disulphonic acid, m.p. 265–266° (decomp.) (chloride, m.p. 198–200°; diamide, m.p. >400°), prepared analogously to (I), is oxidised ($\text{K}_2\text{Cr}_2\text{O}_7$) to 4:5-dichloro-2:7-disulphonaphthalic acid, m.p. 176–177° (decomp.). 3:4-Dibromoacenaphthene-1-sulphonic acid, m.p. 240° (decomp.) (chloride, m.p. 190–191°; amide, m.p. 260–262°), and -1:6-disulphonic acid, m.p. 252° (decomp.) [chloride, m.p. 197–198° (decomp.); amide, m.p. 274–275°], and 4:5-dibromo-2-sulpho-, m.p. 235–236°, and -2:7-disulpho-naphthalic acid, m.p. 159–160°, were prepared analogously. R. T.

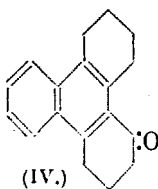
Dehydration of cholesterol. J. C. ECK and R. L. VAN PEURSEM (Iowa State Coll. J. Sci., 1939, 13, 115–128).—Cholesterol (I) when warmed (65°) briefly (3 min.) with 1:1 (vol.) H_2O – H_2SO_4 affords *a*- (II), m.p. 344° (block), 240–265° (decomp.) (tube) (lit. 240°; 260° after sintering at 210–220°), $[\alpha]_{\text{D}}^{25} +96.85$ in CCl_4 , and *c*- (III), m.p. 200° (block), 144–172° (decomp.) (tube) (lit. 127°), $[\alpha]_{\text{D}}^{25} +34.5$ in CCl_4 , but no *b*-cholesterylene. (I) with Br– CHCl_3 and (II)

with Br–AcOH– Et_2O yield bromides, m.p. 245° (block) and 235° (block), respectively, with evolution of HBr. (II) is also formed from (I), cholesterylene (IV), cholesteryl acetate, and cholesterol Bu ether, but not from cholestene, cholesteryl chloride, and dicholesteryl ether (V), with AcOH– H_2SO_4 at 85–90°. (II) may be related to *i*-cholesterol, from which it is obtained [but not from (I)] by Ac_2O – H_2SO_4 at 85–90°. Other conditions for the prep. of (II) are given. A detailed review of the literature is given and it is suggested that $\Delta^{2:4}$ -cholestadiene, (II), (III), (IV), and (V) should be regarded as different dehydration products of (I). J. L. D.

Synthesis of derivatives of chrysene. W. E. BACHMANN and W. S. STRUVE (J. Org. Chem., 1939, 4, 456–463; cf. A., 1936, 1380).—Clemmensen reduction of β -2-phenanthrolylbutyric acid leads to γ -2-phenanthryl- β -methylbutyric acid, m.p. 127.5–129°, cyclised by SOCl_2 in Et_2O containing a little $\text{C}_5\text{H}_5\text{N}$ followed by SnCl_4 in dry C_6H_6 at 0° to 6-*keto*-4-methyl-3:4:5:6-tetrahydrochrysene, m.p. 141–142°, which is reduced to 4-methyl-3:4:5:6-tetrahydrochrysene, thin leaflets or thin prisms, m.p. 141.5–142° (hemipicrate, $2\text{C}_{19}\text{H}_{18}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m.p. 145.5–146°); this is dehydrogenated by Pd–C at 300–320° to 4-methylchrysene, m.p. 229–230° (corr.) (rather unstable picrate, m.p. 143–146°). 2-*n*-Propylphenanthrene, obtained by reduction of the propionyl derivative, has m.p. 35–36° (picrate, m.p. 92–93°). Non-cryst. 3-*n*-propylphenanthrene and its picrate, m.p. 107–108°, are described. β -2:9:10-Dihydrophenanthrolylpropionic acid, Zn–Hg, AcOH, conc. HCl, and PhMe yield γ -2:9:10-dihydrophenanthrylbutyric acid, m.p. 91–92°, which is esterified with MeOH, dehydrogenated by Pd–C at 240–260°, and then hydrolysed to γ -2-phenanthrylbutyric acid, m.p. 133–134°. This is cyclised to 6-*keto*-3:4:5:6-tetrahydrochrysene (I), m.p. 125–126°, which is transformed by MgMeI in Et_2O – C_6H_6 into 6-hydroxy-6-methyl-3:4:5:6-tetrahydrochrysene, m.p. 124–125°, converted by Pd–C at 300–320° into 6-methylchrysene, m.p. 151–151.2° (corr.) (picrate, m.p. 134–135°). $\text{Al}(\text{OPr}^i)_3$ reduces (I) to 6-hydroxy-3:4:5:6-tetrahydrochrysene (II), m.p. 160–162°, which yields a *Me* ether, m.p. 79–80.5°, and an acetate, m.p. 119–120.5°. Dry HCl transforms (II) suspended in dry C_6H_6 containing CaCl_2 at room temp. into 6-chloro-3:4:5:6-tetrahydrochrysene, m.p. 115–117° (decomp.) and, after re-solidification, m.p. 174–178°, which is transformed by boiling $\text{C}_5\text{H}_5\text{N}$ into 3:4-dihydrochrysene (III), m.p. 182.5–184.5° (picrate, m.p. 155–156°). (I) is reduced (Clemmensen) to 3:4:5:6-tetrahydrochrysene, m.p. 180.5–181.5° (picrate, m.p. 134–135.5°), which, like (III), is dehydrogenated by Pd–C in N_2 at 300–320° to chrysene. H. W.

Reactions of tetrahydrophenanthrene. Synthesis of triphenylene and methyltriphenylene. W. E. BACHMANN and W. S. STRUVE (J. Org. Chem., 1939, 4, 472–479).— C_{10}H_8 , $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 give a mixture of β -1- and -2-naphthoylethylpropionic acid which is reduced (Clemmensen) and then cyclised by SOCl_2 in abs. Et_2O containing a little $\text{C}_5\text{H}_5\text{N}$ followed by SnCl_4 in C_6H_6 at 0° to 1- and 4-*keto*-1:2:3:4-tetrahydrophenanthrene, which are

converted (Clemmensen) into 1:2:3:4-tetrahydrophenanthrene (I), m.p. 32.5–33.5°. AcCl , (I), and AlCl_3 afford 9-acetyl-1:2:3:4-tetrahydrophenanthrene (II), m.p. 56.5–58°, dehydrogenated by S at 210–220° to 9-acetylphenanthrene. Addition of $1\text{-C}_{10}\text{H}_7\text{Et}$ to a solution of $(\text{CH}_3\text{CO})_2\text{O}$ and AlCl_3 in PhNO_2 at 0° gives β -4-ethyl-1-naphthoylethylpropionic acid, m.p. 129.5–131°, reduced by Zn-Hg , AcOH , and conc. HCl in presence of PhMe to γ -4-ethyl-1-naphthylbutyric acid, m.p. 115–116.5°. This is cyclised to 1-keto-9-ethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 52–53°, which is reduced (Clemmensen) to 9-ethyl-1:2:3:4-tetrahydrophenanthrene, m.p. 23–25° (picrate, m.p. 125.5–126.5°), also obtained similarly from (II); it is dehydrogenated (Pd-C at 300–320°) to 9-ethylphenanthrene, m.p. 63.5–64.5° (picrate, m.p. 120.5–122.5°). (II) is converted by Br in well-cooled Et_2O into 9-bromoacetyl-1:2:3:4-tetrahydrophenanthrene, m.p. 90.5–91.5°; this is condensed with $\text{CHNa}(\text{CO}_2\text{Et})_2$ in C_6H_6 and the product is hydrolysed and then decarboxylated to β -9-1:2:3:4-tetrahydrophenanthroylethylpropionic acid, m.p. 167.5–169°, also obtained from (I), $(\text{CH}_3\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 . This is reduced to γ -9-1:2:3:4-tetrahydrophenanthrylbutyric acid (III), m.p. 133–134°, the Me ester of which is dehydrogenated (Pd-C at 250–270°) and then hydrolysed to γ -9-phenanthrylbutyric acid, m.p. 171–172°.



(IV.)

(III) is cyclised to 1-keto-1:2:3:4:9:10:11:12-octahydrotriphenylene (IV), m.p. 121–122°, whence 1:2:3:4:9:10:11:12-octahydrotriphenylene, m.p. 120.5–122° (picrate, m.p. 193–195°), which is dehydrogenated (Pd-C at 300–320°) to triphenylene, m.p. 196.5–197.5°. MgMeI and (IV) in $\text{Et}_2\text{O-C}_6\text{H}_6$ yield 1-hydroxy-1-methyl-1:2:3:4:9:10:11:12-octahydrotriphenylene, m.p. 104–105°, dehydrated and dehydrogenated (Pd-C at 300–320°) to 1-methyltriphenylene, m.p. 93–94° (picrate, m.p. 172.5–174°). H. W.

Methyl homologues of triphenylene. L. F. FIESER and L. M. JOSHEL (J. Amer. Chem. Soc., 1939, 61, 2958–2961).— γ -Keto- γ -9-phenanthryl-n-butylbutyric acid [prep. from Mg 9-phenanthryl bromide (I) and $(\text{CH}_3\text{CO})_2\text{O}$ improved to give a 45% yield], m.p. 179.5–180.5° (Me ester, new m.p. 88.6–89.4°, does not condense with MgMeCl or MgMeI), and Zn-Hg-PhMe-HCl give γ -9-phenanthryl-n-butylbutyric acid (79%), m.p. 172.8–174°, cyclised by anhyd. HF at 0° to 87% of 1-keto-1:2:3:4-tetrahydrotriphenylene, m.p. 97–99°. With MgMeCl this gives a carbinol, which by dehydration by I at 200–220° and subsequent heating with S at 230° and then at 230–250° gives 1-methyltriphenylene (42.5%), m.p. 93.4–94.2° (picrate, m.p. 177.2–178.2°). With methylsuccinic anhydride, (I) yields similarly γ -keto- γ -9-phenanthryl- α -methyl-n-butylbutyric acid (33%), m.p. 155–156° (structure proved by conversion by Br-CHCl_3 , followed by $\text{NaOH-EtOH-H}_2\text{O}$, into 9-acetophenanthrene), γ -9-phenanthryl- α -methyl-n-butylbutyric acid, m.p. 136.6–137.4°, and 1-keto-2-methyl-1:2:3:4-tetrahydrotriphenylene (II), m.p. 85–86.5°. Zn-Hg-PhMe-HCl and (II) give 2-methyl-1:2:3:4-tetrahydrotriphenylene, m.p. 116.2–116.8°, converted by

Pd-C-N_2 at 215–230° and then at 310° into 2-methyltriphenylene, m.p. 102.6–103.6° (picrate, m.p. 192.4–193°), which is also obtained directly from (II) by Pd-C-N_2 at 300–310°. With MgMeCl in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$, (II) gives a crude carbinol, converted by Pd-C at 290–315° into 1:2-dimethyltriphenylene, m.p. 86.8–87.4° (picrate, m.p. 154–155°). $\text{OMe-CH}_2\text{CN}$ and (I) in boiling C_6H_6 give 9-phenanthryl methoxymethyl ketone, m.p. 67.2–68°, b.p. 220–225°/3 mm., converted by MgMeCl in C_6H_6 at room temp. into α -9-phenanthryl- β -methoxyisopropyl alcohol, m.p. <0°, b.p. 192–195°/1 mm. KHSO_4 at 180° then yields α -9-phenanthrylpropaldehyde, m.p. 65.5–67.6°, which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and a little piperidine in $\text{C}_5\text{H}_5\text{N}$ at 100° gives γ -9-phenanthryl- Δ^4 -pentenoic acid, m.p. 178.8–179.4° (softens at 173°), hydrogenated (PtO_2 ; AcOH) to γ -9-phenanthryl-n-valeric acid, m.p. 83–85°. This is cyclised by IHF at room temp. to 1-keto-4-methyl-1:2:3:4-tetrahydrotriphenylene (82%), m.p. 99–100.5°, which affords (Grignard reaction; I ; S) 1:4-dimethyltriphenylene (35%), m.p. 108.4–109.2° (picrate, m.p. 148.4–149.4°). M.p. are corr.

R. S. C.

Syntheses of picene. N. L. DRAKE and W. C. McVEY (J. Org. Chem., 1939, 4, 464–471).— C_{10}H_8 and $(\text{CH}_3\text{CO})_2\text{O}$ are condensed to a mixture of β -1- and -2-naphthoylethylpropionic acids, the separation of which is described. γ -1-Naphthylbutyric acid in C_6H_6 is converted by successive treatments with PCl_5 and AlCl_3 into 1-keto-1:2:3:4-tetrahydrophenanthrene (I), b.p. 145–150°/1 mm., m.p. 95–96° [2:4-dinitrophenylhydrazones, m.p. 283–285° (decomp.)]. *o*- and *p*- $\text{C}_6\text{H}_4\text{Me-MgBr}$ and $(\text{CH}_2)_2\text{O}$ yield β -*o*-, b.p. 99–105°/1 mm. (3:5-dinitrobenzoate, m.p. 126–128°), and β -*p*-tolylethyl alcohol, b.p. 100–106°/1 mm., 235°/atm. pressure (3:5-dinitrobenzoate, m.p. 147–149°), respectively, converted by SOCl_2 and NPhMe_2 into the respective chlorides, b.p. 80–84°/1 mm., 223°/atm. pressure, and b.p. 81–85°/1 mm., 222°/atm. pressure. $\text{CH}_2\text{Ph-CH}_2\text{-MgBr}$ and (I) in $\text{Et}_2\text{O-C}_6\text{H}_6$ (1:1) afford 1-phenylethyl-3:4-dihydrophenanthrene (II), b.p. 185–187°/0.5–1 mm., m.p. 62–63° [additive compound, m.p. 91–92°, with $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$]. Similarly prepared are 1- β -*o*- (III), b.p. 190–195°/0.5–1 mm. [additive compound, m.p. 101.5–102.5°, with $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$], and 1- β -*p*- (IV), b.p. 200–205°/0.5–1 mm., m.p. 79.5–81° (picrate, m.p. 101–102°), -tolylethyl-3:4-dihydrophenanthrene. (II) is dehydrogenated by Pd-C at 270–320° to 1-phenylethylphenanthrene, m.p. 86.5–89.5° [additive compound (1:2), m.p. 149–151° with $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$], which yields only tarry material from which picene (V) cannot be extracted when cyclisation is attempted with AlCl_3 in CS_2 at the b.p. or at a lower temp. Cyclisation of (II) by AlCl_3 in CS_2 at 0–5° gives a pasty product which does not give a compound with 2:4:6- $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ or $s\text{-C}_6\text{H}_3(\text{NO}_2)_2$; it is dehydrogenated by Pd-C at 390–400° to 1% of (V), m.p. 367–368.5°, which is also obtained by a similar procedure from (III). (IV) could not be converted into (V). H. W.

Synthesis of rubicene from fluorenone, using metallic calcium. V. I. CHMELEVSKI and G. I. FEDOROV (J. Gen. Chem. Russ., 1939, 9, 1423—

1425).—Fluorenone and Ca when heated give rubicene in 13% yield. 9 : 10-Diphenylanthracene is obtained analogously from COPh_2 (20% yield). R. T.

Hydroxy-derivatives of diphenylethylamine. A. LESPAGNOL, J. TURLUR, and L. LESPAGNOL (Bull. Sci. Pharmacol., 1939, 44, 305—311).— $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{o-C}_6\text{H}_4(\text{OII})_2$, and ZnCl_2 at 150° yield 3 : 4-dihydroxydeoxybenzoin, the *oxime*, m.p. 83° , of which is reduced (Na-Hg , EtOH-AcOH) to β -phenyl- α -3 : 4-dihydroxyphenylethylamine, m.p. 135° (hydrochloride, m.p. 186°). The *oxime*, m.p. $121-122^\circ$, of 4'-hydroxydeoxybenzoin (I) similarly yields α -phenyl- β -p-hydroxyphenylethylamine, m.p. 159° . 4-Nitrobenzil is reduced (Sn , aq. EtOH-HCl) to 4'-aminodeoxybenzoin [hydrochloride, m.p. 265° (decomp.)], converted (diazomethod) into (I). R. T.

Kinetics of reaction of o-chloronitrobenzene with aqueous ammonia.—See A., 1939, I, 616.

Alkanolamines. VII. Condensation products of monoethanolamine and the isomeric dichloronitrobenzenes. C. B. KREMER and A. BENDICH (J. Amer. Chem. Soc., 1939, 61, 2658—2661; cf. A., 1939, II, 366).—Nitration of 2 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$ gives at best very poor yields. $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ and HCl-KClO_3 at 70° give varying amounts of 4 : 2 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$ and 4 : 2 : 6 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$, the latter product being converted by a diazo-reaction into 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$, m.p. 65° . Sn-HCl then gives 3 : 5 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$, m.p. 51° , the Ac derivative, m.p. 186° , of which with HNO_3 (d 1.51) yields 4 : 3 : 5 : 1- (I), m.p. 222° , and 2 : 3 : 5 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NHAc}$ (II), m.p. 138° . Hydrolysis (conc. H_2SO_4 at 110°) and a subsequent diazo-reaction convert (I) into 2 : 6 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$, m.p. 70.5° , b.p. $100-101^\circ/4-5$ mm., and (II) into 2 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$, m.p. 34° , b.p. $105-107^\circ/3-4$ mm. $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ and HNO_3 (d 1.5) at 20° give (mainly) 2 : 3 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NHAc}$, m.p. $186-187^\circ$, and thence (with H_2SO_4 at 110°) 2 : 3 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}_2$, m.p. 127° , and (diazo-reaction) 1 : 2 : 3- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$, m.p. 61° . Condensation of the appropriate $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$ in boiling BuOH with 2—3 mols. of $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{OH}$ or slightly >1 mol. in presence of MgO (1 mol.) gives 6-, b.p. $155-157^\circ/2$ mm., 5-, m.p. 116° [also from 1 : 3 : 4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$], 4-, m.p. 107.5° , and 3-chloro-2-nitro-, m.p. 78.5° , and 6-chloro-4-nitro-N- β -hydroxyethylamine, m.p. 120° , reduced by alkaline $\text{Na}_2\text{S}_2\text{O}_4$ to 6-, b.p. $135-137^\circ/2$ mm., 5-, m.p. 104.5° , 4-, m.p. 122.5° , and 3-chloro-2-amino-, m.p. 74° , and 6-chloro-4-amino-N- β -hydroxyethylamine, decomp. $185^\circ/1$ mm. 2 : 6 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$ is the least reactive isomeric. 2 : 5 : 1- is more reactive than 3 : 4 : 1- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NO}_2$. M.p. are corr. R. S. C.

Separated auxo-enoid systems. VII. Influence of a second auxo-group on the coloration of nitrobenzylarylamines. V. A. IZMAILSKI and V. I. STAVROVSKAJA (J. Gen. Chem. Russ., 1939, 9, 1007—1014).—*m*- or *p*-Substitution in the Ph of 2 : 4 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NHPh}$ has a bathochromic effect, the auxochromes being $\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{R}$ ($\text{R} = m$ - or *p*-Me or -NHAc). The following compounds are described : 2 : 4-dinitrobenzyl-*m*-, m.p. 86° , and

p-toluidine, m.p. 101° (lit. 93°), *m*-, m.p. 136° , and *p*-acetamidoaniline, m.p. 131° . R. T.

[Condensation of] aromatic amines and 2-bromo-5 : ω -dinitrostyrene. D. E. WORRALL and J. FINKEL (J. Amer. Chem. Soc., 1939, 61, 2969—2970).— $\text{o-C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, MeNO_2 , and NEt_3 at $25-30^\circ$ give *o*-bromo- ω -nitrostyrene (I), m.p. 84° , which with fuming HNO_3 gives 2-bromo-5 : ω -dinitrostyrene (II), m.p. $144-145^\circ$, oxidised by KMnO_4 to 5 : 2 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$. The corresponding chlorodinitro compound was previously (A., 1939, II, 57) wrongly named. With Br, followed by warm KOAc-EtOH , (II) gives 2 : ω -dibromo-5 : ω -dinitrostyrene (III), m.p. $146-147^\circ$ (corresponding ω -chloro-2-bromo-compound, m.p. $140-141^\circ$). By adding the appropriate amine in hot EtOH , (II) gives α -nitro- β -o-, m.p. $108-109^\circ$, *m*-, m.p. $103-104^\circ$, and *p*-toluidino-, m.p. $132-133^\circ$, *o*-, m.p. $139-140^\circ$, *m*-, m.p. $159-160^\circ$ (?), and *p*-anisidino-, m.p. $105-106^\circ$, *p*-phenetidino-, m.p. $134-135^\circ$, *p*-dimethylaminoanilino-, m.p. $140-141^\circ$, and *p*-phenylhydrazino- β -2-bromo-5-nitrophenylethane, m.p. $147-148^\circ$, and NN' -di-(β -nitro- α -2-bromo-5-nitrophenylethyl)-amine, m.p. $146-147^\circ$, *p*-phenylenediamine, and *benzidine*, m.p. indefinite. Similarly, (I) gives NN' -di-(β -nitro- α -o-bromophenylethyl)-*p*-phenylenediamine, m.p. $146-147^\circ$, and (III) gives a similar product, m.p. indefinite. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ adds to (III), yielding a product, m.p. $103-104^\circ$. R. S. C.

Structure of naphthalene, hydrindene, and tetrahydronaphthalene derivatives. R. B. SANDIN and T. H. EVANS (J. Amer. Chem. Soc., 1939, 61, 2916—2919).—Fixation of ethylenic linkings in aromatic compounds may be judged by the relative lability of Br (replacement by H on treatment with $\text{SnCl}_2\text{-HCl}$) in bromo-hydroxy- and -amino-derivatives, lability being caused by separation of the Br from OH or NH_2 by an ethylenic linking or a conjugated system. Results with 1 : 2-, 4 : 1-, and 3 : 2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NH}_2$ and 1 : 3 : 2- $\text{C}_{10}\text{H}_5\text{Br}_2\cdot\text{NH}_2$ indicate stability of the Erlenmeyer system, which is also borne out by the results of Franzen *et al.* (A., 1920, i, 730; 1922, i, 450). Results with 4 : 6-dibromo-5-amino- (I) and 4-bromo-5-amino-hydrindene [prep. from (I) by $\text{SnCl}_2\text{-HCl}$], m.p. $54-55^\circ$, favour the Mills-Nixon formula. Br is removed fairly readily from 5-bromo-6-amino-1 : 2 : 3 : 4-tetrahydronaphthalene. Fairly ready removal of Br from *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ favours existence of both Kékulé or resonating forms. R. S. C.

Steric nature of the ortho effect in the hydrogen exchange reactions of aromatic tertiary amines.—See A., 1939, I, 617.

Cleavage of quaternary ammonium salts by sodium sulphide. II. H. R. SNYDER and J. C. SPECK (J. Amer. Chem. Soc., 1939, 61, 2895—2897; cf. A., 1939, II, 207).— $\text{CH}_2\text{Ph}\cdot\text{NR}_3\text{Cl}$ are decomposed by Na_2S most readily if the N carries or is part of an aromatic ring, but even more stable salts decompose at higher temp. With hot, aq. Na_2S , $\text{CH}_2\text{Ph}\cdot\text{NMe}_3\text{Br}$, NPhMe_3I , and NBu^4I are unaffected; cyclohexylbenzyl-diethylammonium chloride, m.p. 179° (decomp.), is only slightly affected, $(\text{CH}_2\text{Ph})_2\text{NEt}_2\text{I}$ gives only 3% of $(\text{CH}_2\text{Ph})_2\text{S}$ (I) in 3 hr., and benzylpyridinium

chloride gives 65% of C_5H_5N and 69% of (I). $CH_2Ph \cdot NMe_3Br$ with $Na_2S_9H_2O$ in $(OH \cdot [CH_2]_2)_2O$ at $135-150^\circ$ gives 54% of NMe_3 and 47% of (I). NBu^a_4I at 175° similarly gives 70% of NBu^a_3 . *Phenyltrimethylammonium bromide*, hygroscopic, and aq. Na_2S give 41% of $NPhMe_2$ and 44% of $(CH_2 \cdot CH \cdot CH_2)_2S$. $CH_2Ph \cdot NPhMe_2Cl$ and boiling, aq. $Na_2S_2O_4$ give 58% of $NPhMe_2$ and 60% of $CH_2Ph \cdot S \cdot SO_3NPhMe_2 \cdot CH_2Ph$, possibly owing to prior hydrolysis of the $Na_2S_2O_4$ to $Na_2S_2O_3$ and $NaHSO_3$.

R. S. C.

Preparation of sulphanilamide. O. BAINE (J. Chem. Educ., 1939, 16, 278).—The reactions involved in the synthesis of the amide from NH_2Ph are discussed. The prep. is suitable as a laboratory experiment.

L. S. T.

Purification of *p*-acetamidobenzenesulphonyl chloride. L. H. PENCE and H. C. WINTER (J. Amer. Chem. Soc., 1939, 61, 2977–2978).—*p*- $NHAc \cdot C_6H_4 \cdot SO_2Cl$ (70) (stable if pure), from $NHPhAc$ (67.5) and $ClSO_3H$ (290 g.), is obtained pure by suitable crystallisation from $Et_2O + C_6H_6$.

R. S. C.

Sulphanilamide derivatives. IV. N^1N^4 -Diacyl- and N^1 -acyl-sulphanilamides. M. L. CROSSLEY, E. H. NORTHEY, and M. E. HULTQUIST (J. Amer. Chem. Soc., 1939, 61, 2950–2955; cf. A., 1938, II, 439).— N^1 -Acylsulphanilamides are prepared, usually best by condensing *p*- $NHAc \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ (I) with $RCOCl$ in C_5H_5N at $100-110^\circ$ (less well in boiling $PhMe$ etc.) and hydrolysing the diacyl derivative by boiling with a slight excess of aq. $NaOH$. Alternatively, (I) is heated with $(RCO)_2O$ at $70-80^\circ$ or the Na derivative of (I) is heated with $RCOCl$ in dioxan or C_5H_5N . The following are described. N^1N^4 -Diacetylsulphanilamide, new m.p. $253.5-255^\circ$; N^1 -acetyl- N^1 -propionyl-, m.p. $242.5-244.3^\circ$, -n-, m.p. $238.2-240^\circ$, and -iso-butyl-, m.p. $247-248^\circ$, -iso-valeryl-, m.p. $215-217.5^\circ$, - β -ethylbutyl-, m.p. $270-272^\circ$, -hexoyl-, m.p. $191-193^\circ$, -heptoyl-, m.p. $205-207.5^\circ$, - β -ethylhexoyl-, m.p. $214-215.6^\circ$ (Na and Mg salts), -octoyl-, m.p. $195-197.6^\circ$, -decoyl-, m.p. $143.2-144.8^\circ$, -undecoyl-, m.p. $153.2-155^\circ$, -dodecoyl-, m.p. $130-136^\circ$, -tetradecoyl-, m.p. $144.2-145^\circ$, - Δ^1 -octadecenoyl-, m.p. $131-135^\circ$, -chaulmoogryl-, -benzoyl-, m.p. $280-285^\circ$, -hexahydrobenzoyl-, m.p. $210-222^\circ$, -*p*-nitrobenzoyl-, m.p. $270-272^\circ$, -*p*-aminobenzoyl-, m.p. $260-263^\circ$, - β -phenylpropionyl-, m.p. $202.8-205.4^\circ$ (sinters at 160°), -cinnamoyl-, m.p. $228-229.5^\circ$, -diphenylacetyl-, m.p. $248.5-251^\circ$, -2'-furoyl-, m.p. $240.5-241.5^\circ$, -2'-phenylcinchoninyl-, m.p. $166-170^\circ$, and -nicotinyl-, m.p. $295-300^\circ$, -sulphanilamide; N^1N^4 -didodecoylsulphanilamide, m.p. $144-145^\circ$; N^4 -*p*-acetamidobenzenesulphonyl-, m.p. $150-152^\circ$ (sinters at 120°), and N^4 -sulphanilyl-, m.p. $102-104^\circ$, - N^1 -dodecoylsulphanilamide; N^1 -acetyl-, m.p. $182-184^\circ$ (Na, + H_2O , NH_4 , and NH_2Et_2 salts), -propionyl-, m.p. $134-135^\circ$, -n-, m.p. $125.4-126.6^\circ$, and -iso-butyl-, m.p. $198.5-200^\circ$, - β -ethylbutyl-, m.p. $189-193.5^\circ$, -hexoyl-, m.p. $129.2-129.9^\circ$, -heptoyl-, m.p. $121.8-123.6^\circ$, - β -ethylhexoyl-, m.p. $165.5-168^\circ$, -octoyl-, m.p. $101-103^\circ$, -decoyl-, m.p. $119-121^\circ$, -undecoyl-, dimorphic, m.p. $112.5-114.5^\circ$ and 115° , -dodecoyl- (II), m.p. $127-128.5^\circ$ (*Ag*, *Hg*^{II}, and *Ca*

salts), -tetradecoyl-, m.p. $113.5-117.7^\circ$, -octadecoyl- (crude), m.p. $98-102^\circ$, - Δ^1 -octadecenoyl-, amorphous, -hexahydrobenzoyl-, m.p. $198.5-200^\circ$, -chaulmoogryl-, m.p. $97.9-99^\circ$, -benzoyl-, m.p. $181.2-182.3^\circ$, -*p*-nitrobenzoyl-, m.p. $235-240^\circ$, -*p*-aminobenzoyl-, m.p. $197.8-199^\circ$, - β -phenylpropionyl-, m.p. $160.3-161.5^\circ$, -cinnamoyl-, forms, (a), m.p. $174-175^\circ$, and (b), m.p. 145° (immediate; resolidifies) (sinters at 130°), -*p*-carboxybenzoyl-, m.p. $>225^\circ$ (decomp.), -mandelyl-, m.p. $192.5-194.5^\circ$ (decomp.), -diphenylacetyl-, m.p. $210.5-212^\circ$, -2'-furoyl-, m.p. $191.5-192^\circ$, -2'-phenylcinchoninyl-, m.p. $305-310^\circ$, -nicotinyl-, m.p. $256-257.5^\circ$, and -3'-hydroxy-2'-naphthoyl-, m.p. $245-250^\circ$, -sulphanilamide. Acylation of the appropriate nitrobenzenesulphonamide and subsequent reduction by $Fe-AcOH$ yields N^1 -acetyl-, m.p. $153.5-155^\circ$, and -tetradecoyl-metanilamide, m.p. $113.5-114.2^\circ$, and N^1 -dodecoylsulphanilmethylamide, m.p. $59.3-60.5^\circ$. The long-chain amides are sol. in fats and their absorption after oral administration is accelerated by feeding fats. (II) is at least as effective as *p*- $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ against various β -haemolytic streptococci in mice and very effective in preventing spread of mycobacterium tuberculosis in guinea-pigs.

R. S. C.

Para- and dia-magnetic tetramminnickel salts of phenylethylenediamines.—See A., 1939, I, 624.

Colour and dyeing properties of alkyl, alkoxy-, and aryloxy-derivatives of aminoazobenzene. J. C. EARL and A. O. ROBSON (J. Proc. Austral. Chem. Inst., 1939, 6, 268–278).—By coupling diazotised NH_2R with NH_2R' , the following are prepared: 4-dimethylamino-2'-methyl-, m.p. $67-68^\circ$ (all m.p. corr.), and -2:2'-dimethyl-, m.p. $79-80^\circ$, 3:2'-dinitro-4-amino-, m.p. $199-200^\circ$, and 4-amino-2:3'-dimethoxy-, m.p. $165-166^\circ$ (from *m*- $OMe \cdot C_6H_4 \cdot NH_2$ diazotised by $NaNO_2-AcOH$ in presence of $K_2C_2O_4$ and saponin), -2-phenoxy-, m.p. $129-130^\circ$, and -2-methoxy-azobenzene, m.p. $160-161^\circ$. The extinction coeffs. (λ of heads of bands recorded) and dyeing properties of these and 6 other aminoazo-compounds show that a 2-substituent in the 4- NH_2 -ring has the most pronounced effect and causes colour-deepening in the order $OMe > Me > OPh$; NO_2 or Cl in this position has a lightening effect. Diazotised NH_2Ph and (?) *m*- $NH_2 \cdot C_6H_4 \cdot O \cdot C_{10}H_7$ give a compound, m.p. $90-91^\circ$, which is not 4-amino-2-naphthoxyazobenzene.

E. W. W.

Alleged isomerism of α - and β -*p*-azophenol. W. M. LAUER, H. P. KLUG, and S. A. HARRISON (J. Amer. Chem. Soc., 1939, 61, 2775–2779).—The α - and β -forms of *p*-azophenol (I) are shown by X-ray powder photographs, ebullioscopy, and polarographic analysis to be identical and not *cis-trans*-isomerides (cf. Willstätter *et al.*, A., 1907, i, 566). Only one set of derivatives could be prepared, viz., $(NO_2)_2$ - (prep. by conc. HNO_3-AcOH at 0°), m.p. $235-236^\circ$, $(NO_2)_4$ - (prep. by fuming HNO_3-AcOH at $<0^\circ$), m.p. $261-262^\circ$ (decomp.), Br_4 -, m.p. $273-274^\circ$ (diacetate, m.p. $263-264^\circ$), dibenzoate, m.p. $297-298^\circ$, and dibromodinitro-derivative, m.p. $281-282^\circ$. (I) exists in hydrated and green and red anhyd. forms.

R. S. C.

Diazo-chemistry. H. H. HODGSON (Rec. trav. chim., 1939, 58, 928—930).—Controversial with Schoutissen (A., 1939, II, 209). A. T. P.

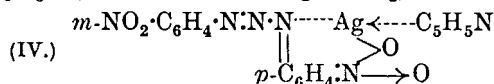
Preparation of diazo-compounds through the agency of organo-metallic derivatives. L. G. MARKOVA and A. N. NESMEJANOV (J. Gen. Chem. Russ., 1939, 9, 771—779).—The action of $\text{NO-N}_2\text{O}_3$ on aromatic organo-metallic compounds leads to the formation of diazonium nitrates: $2\text{N}_2\text{O}_3 \rightarrow \text{N}_2\text{O}_4 + 2\text{NO}$; $\text{MPh}_2 + 2\text{N}_2\text{O}_4 \rightarrow 2\text{PhNO} + \text{M}(\text{NO}_3)_2$; $\text{PhNO} + 2\text{NO} \rightarrow \text{PhN}_2\text{NO}_3$. The following were studied (yield of diazonium nitrate in parentheses): HgPh_2 (85%); $\text{HgPh}\cdot\text{OAc}$ (quant.); SnPh_4 (40%); SnPh_3Cl (48%); SnPh_2Cl_2 (49%); SnPhCl_3 (80%); PbPh_4 (quant.); PbPh_3Cl (50%); BiPh_3 (54%); TiPh_2Cl (8%); MgPhBr (15%). The yields were considerably reduced by using only N_2O_3 . The diazonium salt was not obtained using LiPh , AsPh_3 , SbPh_3 , PbPh_2Cl_2 , SiPh_4 , and ZnPh_2 . V. A. P.

Structure of diazoamino-salts. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1939, 6, 348—361).—The theory advanced by Mangini *et al.* (A., 1934, 68; 1935, 969) to account for highly coloured forms of metal salts of diazoamino-compounds is untenable, since such forms are actually derived from diazoamino-azo-compounds either present in the starting materials or formed (*e.g.*, under the influence of acid) during the prep. of the salts. Details are given for the prep. of the K and Hg^{II} salts of diazoaminobenzene (I), the Ag salt of 3-nitro- and the Ag (II) and Hg^{II} salts of 4-nitro-diazoaminobenzene. These salts exist in one (yellow) form; (II) dissolves in $\text{C}_5\text{H}_5\text{N}$ to a red solution (see following abstract). The Hg^{II} salt of diazoaminoazobenzene and the Ag salts of 3- and 4-nitrobenzenediazoaminoazobenzene are all red (varying shades). 2:2'-Dinitrodiazoaminobenzene (in COMe_2) with $\text{C}_5\text{H}_5\text{N-MeOH-AgNO}_3 + \text{NaOAc}$ gives a red (aci) Ag salt (+ $\text{C}_5\text{H}_5\text{N}$), which loses $\text{C}_5\text{H}_5\text{N}$ at $100^\circ/2$ hr. and yields the yellow (triazene) Ag salt. 3:3'-Dinitrodiazoaminobenzene similarly affords only a yellow Ag salt, sol. in hot $\text{C}_5\text{H}_5\text{N}$ to an orange-yellow solution. The above and previous results (A., 1938, II, 483; 1939, II, 152) show that pure (I) and its (nuclear) Me derivatives give no colour with EtOH-alkali and yield only yellow salts. Diazo-amino-compounds with *o*- or *p*- NO_2 give intense colours with alkali and are strongly adsorbed on $\text{Mg}(\text{OH})_2$ with formation of brilliantly coloured lakes; *m*- NO_2 -compounds similarly give an orange colour and are only feebly adsorbed. In all cases, methylation of the labile H causes loss of salt-forming properties. Structures for the different types of salts are elaborated (*cf. loc. cit.*). H. B.

Isomerism of diazoamino-salts. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1939, 6, 362—368).—3:4'-Dinitrodiazoaminobenzene (I), m.p. 225—226° [obtained in small yield from carefully neutralised *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ in $\text{COMe}_2\text{-EtOH-NaOAc}$ (large excess)], is dissolved in EtOH-NaOH and added to $\text{C}_5\text{H}_5\text{N-MeOH-AgNO}_3 + \text{NaOAc}$ at 20° ; the pptd. salt (II) dissolves in hot $\text{C}_5\text{H}_5\text{N}$ to a deep red solution from which EtOH ppts. the pure, yellow (triazene) Ag salt (III). Suitable crystallisation from $\text{C}_5\text{H}_5\text{N}$ at $<-5^\circ$ to -2° affords the scarlet

HH ** (A., II.)

(aci) Ag salt (+ $\text{C}_5\text{H}_5\text{N}$) (IV), which when freed from $\text{C}_5\text{H}_5\text{N}$ (at 100° or in boiling COMe_2) affords a yellow



salt [= (III)] which is a mixture of the two possible isomerides since this with MeI-COMe_2 gives a mixture (A), m.p. $153\text{--}157^\circ$ (shrinks at $145\text{--}146^\circ$), of *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p$ and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\text{-}p$. (A) is also similarly obtained from (I), (II), or (III). Suitable treatment with, and crystallisation from, cold $\text{C}_5\text{H}_5\text{N}$ also affords a scarlet salt (+ $\text{C}_5\text{H}_5\text{N}$) from the yellow Ag salt (V) of 4-nitrodiazoaminobenzene (preceding abstract). Removal of $\text{C}_5\text{H}_5\text{N}$ [as for (IV)] and subsequent methylation show that (V) is a mixture of isomerides since a mixture (B), m.p. $94\text{--}95^\circ$, of *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NPhMe}$ and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{NPh}$ is obtained. Proof of the mixture (B) is afforded by hydrolysis with conc. HCl-CuCl at room temp. whereby PhCl , *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$, and NHPhMe are obtained. H. B.

Mechanism of halogenation of phenols. E. A. SCHILOV (J. Gen. Chem. Russ., 1939, 9, 780—781).—Polemical (*cf.* A., 1938, II, 405). V. A. P.

Reaction between diphenylketen and phenylacetylene. L. I. SMITH and H. H. HOEHN (J. Amer. Chem. Soc., 1939, 61, 2619—2624).—Contrary to Staudinger (Annalen, 1907, 356, 94), CPh_2CH adds CPh_2CO at room temp., giving 3:4-diphenyl- α -naphthol (I), dimorphic, m.p. $143\text{--}144^\circ$ and 154° [positive Folin reaction; 1 active H; acetate, m.p. $162\text{--}162.5^\circ$; Me ether, m.p. $203\text{--}203.5^\circ$ (2- NO_2 -derivative, m.p. 202°)], but in light petroleum reaction is much slower. (I) is sol. in KOH-MeOH and unstable in air. $\text{Pb}(\text{OAc})_4$ in AcOH oxidises (I) to 3:4-diphenyl-1:2-naphthaquinone (II), m.p. $249\text{--}250^\circ$ (phenazine derivative, m.p. $274\text{--}275^\circ$), obtained also in poor yield as sole product by $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-CHCl}_3$, but $\text{K}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ gives BzOH , *o*- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$, and a substance, m.p. $280\text{--}286^\circ$. Zn in $\text{AcOH-H}_2\text{O}$ (10:1) or $\text{Na}_2\text{S}_2\text{O}_4$ reduces (II) to the quinol, which readily regenerates (II) in air, but Zn dust and NaOAc in Ac_2O give 1:2-diacetoxy-3:4-diphenylnaphthalene, m.p. $166\text{--}167^\circ$. With *p*- $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ and NaOAc in AcOH , (I) gives the red 2-azo-compound, reduced by alkaline $\text{Na}_2\text{S}_2\text{O}_4$ to an unstable amine, which is oxidised by FeCl_3 to (II). $\text{Br-Et}_2\text{O}$ converts (I) into the 2-Br-derivative, m.p. $157\text{--}158^\circ$ (acetate, m.p. $199\text{--}200^\circ$; Me ether, m.p. $209\text{--}210^\circ$), which with $\text{CrO}_3\text{-AcOH}$ at 100° yields (II). Franssen's interpretation (A., 1925, i, 1146) of the reaction of 1:4-naphthaquinone and MgPhBr is incorrect; 5 mols. of MgPhBr in Et_2O give 1-hydroxy-4-keto-1:2-diphenyl-1:2:3:4-tetrahydronaphthalene, m.p. 207° (oxime, m.p. $196\text{--}197^\circ$), oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH to (II), BzOH , and *o*- $\text{C}_6\text{H}_4\text{Bz}\cdot\text{CO}_2\text{H}$, dehydrated by a little H_2SO_4 in boiling AcOH to (I) or in boiling Ac_2O to the Ac derivative thereof. R. S. C.

α -Nitro- β -naphthol.—See A., 1939, I, 625.

Bromination of 2-hydroxyanthracene. J. S. JOFFE, L. S. EFROS, and C. N. SCHTSCHEGLOVA (J.

Gen. Chem. Russ., 1939, 9, 1128—1132).—2-Acetoxyanthracene and Br in AcOH at room temp. yield 9-bromo-2-acetoxyanthracene, m.p. 110—112°, oxidised by $K_2Cr_2O_7$ in AcOH to 2-acetoxyanthraquinone, and hydrolysed (dil. NaOH) to 9-bromo-2-hydroxyanthracene, m.p. 112—114° (1-p-nitrobenzeneazo-derivative, m.p. 254°). Bromination of 2-hydroxyanthracene gives 2-hydroxy-1:1':9:2'-dianthrylene oxide and 1:10-dibromo-2-hydroxyanthracene, m.p. 198—199°, which with $p-NO_2 \cdot C_6H_4 \cdot N_2Cl$ gives 10-bromo-2-hydroxy-1-p-nitrobenzeneazoanthracene, m.p. 284°. Acetylation of the bromination product gives 1:10, m.p. 198—199°, and 1:9-dibromo-2-acetoxyanthracene, m.p. 157—159°, both yielding 1-bromo-2-acetoxyanthraquinone, m.p. 174°, when oxidised ($K_2Cr_2O_7$ in AcOH). R. T.

α -Di-p-hydroxyphenylpropane, m.p. 104—105°. Diacenaphthylidene diketone, m.p. 285—286°.—See A., 1939, III, 982.

Diaryls and their derivatives. XXI. Oxidation of α -naphthol. J. S. JOFFE and B. K. KRITSCHEVITZOV. XXII. Diphenanthryl dioxide. J. S. JOFFE (J. Gen. Chem. Russ., 1939, 9, 1136—1142, 1143—1144).—XXI. $\alpha-C_{10}H_7 \cdot OH$ and aq. $FeCl_3$ at 70—80° yield a mixture of 4:4'-dihydroxy-1:1'-(I), m.p. 300° (Ac_2 , m.p. 217°, and 3-mono- and 3:3'-di-p-nitrobenzeneazo-derivatives), and 1:1'-dihydroxy-2:2'-dinaphthyl (II), m.p. 220° (Ac_2 , m.p. 169°, and 4-mono- and 4:4'-di-p-nitrobenzeneazo-derivatives). (I) yields 3:10-dihydroxyperylene when heated with $AlCl_3$. (II) and $ZnCl_2$ similarly give 2:2'-dinaphthyl 1:1'-oxide.

XXII. 2:2'-Dihydroxy-1:1'-diphenanthryl and CaO in C_6H_6 (6 hr. at the b.p.) yield 1:1'-diphenanthryl 2:10':10:2'-dioxide, m.p. 280°. R. T.

Use of tri-iodophenyl ethers for the identification of alkyl halides. R. D. DREW and J. M. STURTEVANT (J. Amer. Chem. Soc., 1939, 61, 2666).—Alkyl bromides are characterised by boiling with 2:4:6:1- $C_6H_2I_3 \cdot OH$ and $NaOEt-EtOH$ (cf. Brenans, A., 1901, i, 643), which give 2:4:6- $C_6H_2I_3 \cdot Pr^B$, m.p. 43°, Me , m.p. 98.5°, Et , m.p. 83.5°, Pr^A , m.p. 82°, Bu^A , m.p. 66°, Bu^B , m.p. 48°, n -amyl, m.p. 47°, n -hexyl, m.p. 44.5°, CH_2Ph , m.p. 122.5°, $[CH_2]_2Ph$, m.p. 88°, $[CH_2]_3Ph$, m.p. 63.5°, $p-NO_2 \cdot C_6H_4 \cdot CH_2$, m.p. 207.5°, $[CH_2]_2OH$, m.p. 137.5°, $CH_2 \cdot CO_2Et$, m.p. 124° (lit. 128.5°), and $CHMe \cdot CO_2Et$ ether, m.p. 80.5°. M.p. are corr. R. S. C.

Molecular compounds of α -naphthyl methyl ether with dinitro-compounds. S. I. BURMISTROV (Trans. Ivanovo Chem. Tech. Inst., 1939, 14—17).—This ether forms equimol. compounds with $m-C_6H_4(NO_2)_2$ (m.p. 57.5°), 1:2:4- $C_6H_3Me(NO_2)_2$ (m.p. 71°), 2:4-dinitrophenol (m.p. 96°), 2:4-dinitroanisole (m.p. 66°), 1:2:4- $C_6H_3Cl(NO_2)_2$ (m.p. 66.5°), and 3:5:4:1- $(NO_2)_2C_6H_2Cl \cdot CO_2H$ (m.p. 124°). R. C.

Condensation of diarylcarbinols with naphthyl ethers. S. I. BURMISTROV (Trans. Ivanovo Chem. Tech. Inst., 1939, 17—20).—By condensation with $ZnCl_2$ in AcOH there have been obtained diphenyl-4-methoxy-1-naphthylmethane, m.p. 151°, phenyl-p-xenyl-4-methoxy-1-naphthylmethane, m.p. 155° (de-

comp.), diphenyl-4-ethoxy-1-naphthylmethane, m.p. 159.5°, phenyl-p-tolyl-4-methoxy-1-naphthylmethane, m.p. 132.5°, phenyl-4-methoxy-1-naphthylmethane, m.p. 161—162°, di-p-xenyl-4-ethoxy-1-naphthylmethane, m.p. 114—116°, and phenyl-p-xenyl-4-ethoxy-1-naphthylmethane, m.p. 163—165°. R. C.

Iodo-derivatives of diphenyl ether. II.

Orientation. R. Q. BREWSTER and H. S. CHOQUILL (J. Amer. Chem. Soc., 1939, 61, 2702—2704; cf. A., 1934, 293).—Halogenation of *o*- (I) and *p*- $OPh \cdot C_6H_4 \cdot OMe$ (II) occurs in position 4' (if free), but nitration is guided by the *OMe* and is homo-nuclear. (II), obtained in 70% yield from $KOPh$ and $p-C_6H_4Br \cdot OMe$ or in 20% yield from $p-OH \cdot C_6H_4 \cdot OMe$ and $PhBr$, is converted by ICl in AcOH at 100° into 4-iodo-4'-methoxydiphenyl ether (III), m.p. 115°, which is also obtained from the 4- NH_2 -derivative by the Sandmeyer reaction. $AlCl_3$, first at 130° and then at 140—150°, converts (II) into *p*- $OPh \cdot C_6H_4 \cdot OH$, m.p. 84°, the benzoate, m.p. 97°, of which with $ICl-AcOH$ at 100° gives 4-iodo-4'-benzoyloxy-, m.p. 122°, and thence (boiling $NaOH$ -aq. $EtOH$) 4-iodo-4'-hydroxy-diphenyl ether, m.p. 116°. 4:3:1- $OMe \cdot C_6H_3(NO_2) \cdot OPh$ (IV), prepared by HNO_3-AcOH in 70% yield, is quantitatively hydrogenated (PtO_2) to 3-amino-4-methoxydiphenyl ether, m.p. 70° (*Ac* derivative, m.p. 148°), which affords (diazo-reactions) 3-iodo- (V), m.p. 76°, and 3-bromo-4-methoxydiphenyl ether (VI), m.p. 55°, b.p. 182—187°/10 mm. ICl and Br convert (VI) and (III), respectively, in AcOH into 3-bromo-4'-iodo-4-methoxydiphenyl ether, m.p. 88°. $ICl-AcOH$ converts (III) or (V) into 3:4'-di-iodo-4-methoxydiphenyl ether (VII), m.p. 101°. $ICl-AcOH$ converts (IV) into 4'-iodo-3-nitro-4-methoxydiphenyl ether, m.p. 92°, obtained also from (III) by HNO_3 (*d* 1.42) in AcOH and reduced by Fe powder in AcOH to 4'-iodo-3-amino-4-methoxydiphenyl ether, m.p. 85° [gives (VII) by a diazo-reaction]. 2-Nitro-4'-methoxydiphenyl ether (VIII), m.p. 77°, is obtained in 70% yield from *o*- $C_6H_4Cl \cdot NO_2$ and *p*- $OH \cdot C_6H_4 \cdot OMe$, and with $ICl-AcOH$ gives 4-iodo-2-nitro-4'-methoxydiphenyl ether, m.p. 70°, and thence (Fe powder; $AcOH$) 4-iodo-2-amino-4'-methoxydiphenyl ether, m.p. 102°. Nitration of (VIII) gives (? 3:2'-dinitro-4-methoxydiphenyl ether, m.p. 132°. 1:2:4- $C_6H_3Cl(NO_2)_2$ and *p*- $OH \cdot C_6H_4 \cdot OMe$ give 2:4-dinitro-4'-methoxydiphenyl ether, m.p. 110°. *o*- $OMe \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot NH_2 \cdot p$ gives (Sandmeyer) 4-iodo-2'-methoxy-, b.p. 228°/28 mm., and thence (HNO_3-AcOH) 4'-iodo-5-nitro-2-methoxydiphenyl ether (IX), m.p. 115°. Nitration of (I) or condensation of $KOPh$ with 2:1:5- $OMe \cdot C_6H_3Br \cdot NO_2$ gives 5-nitro-2-methoxydiphenyl ether, m.p. 72°, previously (Lea *et al.*, A., 1926, 397) considered to be the 6- NO_2 -compound and converted by $ICl-AcOH$ into (IX). 5-Iodo-4'-nitro-2-methoxydiphenyl ether, m.p. 109°, is obtained from *o*- $OMe \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot NO_2 \cdot p$ by ICl or from 2:5:1- $OMe \cdot C_6H_3I \cdot OK$ and *p*- $C_6H_4F \cdot NO_2$. R. S. C.

Labile union of oxygen to carbon. Spontaneous dissociation of dimethoxydiphenylanthracene photo-oxide. C. DUFRAISSE, L. VELLUZ, and (MME.) L. VELLUZ (Compt. rend., 1939, 209, 516—518).—Dissociation of 1:4-dimethoxy-9:10-diphenyl-

anthracene photo-oxide (I) (cf. A., 1939, II, 365) is a unimol. reaction which proceeds regularly up to 33% decomp. and then progressively more slowly, probably due to dissolution of solid (I) in the decomp. product. Decomp. occurs at the same rate even at 140 atm. pressure of O_2 so that the reaction is probably irreversible. (I) separated from a photographic plate by black paper produces an image which indicates that activated O_2 (O_3 or H_2O_2 from moisture present) is probably liberated in the reaction. (I) is luminous in the dark, the luminosity increasing with rise in temp. (cf. A., 1933, 1284). J. L. D.

Manufacture of 4:4'-diaminodiphenyl sulphone and its monoacyl derivatives.—See B., 1939, 1102.

Chemistry and chemotherapy of 4:4'-diaminodiphenyl sulphone, 4-amino-4'-hydroxydiphenyl sulphone, and related compounds. G. W. RAIZISS, L. W. CLEMENCE, M. SEVERAC, and J. C. MOETSCH (J. Amer. Chem. Soc., 1939, 61, 2763—2765).— $p\text{-NO}_2\cdot C_6H_4\cdot S\cdot C_6H_4\cdot NH_2\cdot p$ (prep. from $p\text{-C}_6H_4Cl\cdot NO_2$ and an excess of aq. Na_2S), new m.p. 145° , is reduced by $Sn\text{-HCl}$ to $(p\text{-NH}_2\cdot C_6H_4)_2S$, m.p. 108° , the Ac_2 derivative, new m.p. $223\text{--}224^\circ$, of which with $K_2Cr_2O_7\text{-H}_2SO_4\text{-AcOH}$ gives $(p\text{-NHAc}\cdot C_6H_4)_2SO_2$, new m.p. 285° , hydrolysed (HCl) to $(p\text{-NH}_2\cdot C_6H_4)_2SO_2$ (I), new m.p. 175° . $p\text{-NO}_2\cdot C_6H_4\cdot S\cdot C_6H_4\cdot NHAc\cdot p$, new m.p. 198° , gives 4-nitro-4'-acetamidodiphenyl sulphone, m.p. $229\text{--}230^\circ$, reduced by $SnCl_2\text{-EtOH}$ to 4-amino-4'-acetamidodiphenyl sulphone, m.p. $242\text{--}243^\circ$, which by a diazo-reaction affords 4-amino-4'-hydroxydiphenyl sulphone, m.p. $193\text{--}194^\circ$ (N-Ac, m.p. $274\text{--}275^\circ$, and NO-Ac₂ derivative, m.p. $171\text{--}172^\circ$). (I) is superior, and some of the other products are equal, to sulphanilamide in therapeutic effect.

R. S. C.

Reactions of $\alpha\beta$ -unsaturated cyclic aldehydes and ketones. V. dl-Cryptone and cis- and trans-dl-cryptol. D. T. C. GILLESPIE and A. K. MACBETH (J.C.S., 1939, 1531—1534; cf. A., 1939, II, 165).—dl-Cryptone (prep. from a crude l-cryptone by boiling Et_2O + conc. HCl), b.p. $78^\circ/2\text{--}8$ mm. (semicarbazone, m.p. 188° ; p-nitro-, m.p. $160\text{--}161^\circ$, and 2:4-dinitrophenylhydrazones, m.p. $130\text{--}131^\circ$), and $Al(OPr^i)_3\text{-Pr}^iOH$ (prep. described) give readily trans-, b.p. $90^\circ/4$ mm. [isolated as p-nitrobenzoate, m.p. $76\text{--}5^\circ$; α -naphthyl-, m.p. 136° , and phenylurethane, m.p. 108° ; H phthalate, m.p. $97\text{--}97\text{--}5^\circ$; 3:5-dinitrobenzoate, m.p. 108° ($\alpha\text{-C}_{10}H_7\cdot NH_2$ compound, m.p. 140°)], and with difficulty cis-dl-cryptol, b.p. $86^\circ/6$ mm. [isolated as 3:5-dinitrobenzoate, m.p. $96\text{--}5^\circ$ ($\alpha\text{-C}_{10}H_7\cdot NH_2$ compound, m.p. $102\text{--}104^\circ$); α -naphthylurethane, m.p. $105\text{--}5^\circ$; p-nitrobenzoate, m.p. $34\text{--}5\text{--}35\text{--}5^\circ$]. Structures of the products are proved by hydrogenation (Pd-C) to the known H_2 -derivatives.

R. S. C.

Isomerisation of β -substituted styrene oxides. Effect of degree of unsaturation of the substituent. M. TIFFENEAU and P. K. KURIAKI (Compt. rend., 1939, 209, 465—468; cf. A., 1935, 750; 1937, II, 415; 1939, II, 419).—cycloHexene with $CH_2Ph\cdot COCl$ in presence of $SnCl_4$ gives cyclohexenyl benzyl ketone, m.p. 54° , b.p. $192\text{--}194^\circ/25$ mm. (semicarbazone, m.p. 167° ; oxime, m.p. 118°), con-

verted by $Al(OPr^i)_3$ into α -cyclohexenyl- β -phenylethyl alcohol, b.p. $149\text{--}151^\circ/7$ mm. (p-nitrobenzoate, m.p. 79°), dehydrated (H_2SO_4 on pumice) to α -cyclohexenyl- β -phenylethylene, b.p. $137^\circ/5$ mm., which with $NH_2\cdot CO\cdot NHCl$ in aq. AcOH gives a chlorohydrin, converted by KOH into α -cyclohexenyl- β -phenylethylene oxide (I), b.p. $147\text{--}150^\circ/7$ mm. (I) with hot $MgBr_2$ etherate gives cyclohexenylphenylacetaldehyde, b.p. $150\text{--}152^\circ/10$ mm. (semicarbazone, m.p. 203° ; oxime, m.p. 156°), oxidised (Ag_2O) to the corresponding acid, m.p. 162° , which is reduced ($H_2\text{-Raney Ni}$) to cyclohexylphenylacetic acid (II), m.p. 150° . cyclo-Hexylphenylcarbinol with $SOCl_2$ gives the chloride, m.p. 27° , b.p. $153\text{--}154^\circ/15$ mm., the Mg derivative of which with CO_2 gives (II). β -cycloHexyl- α -phenylethyl alcohol, b.p. $156\text{--}157^\circ/17$ mm. (from PhCHO and Mg cyclohexylmethyl iodide), with H_2SO_4 gives α -cyclohexyl- β -phenylethylene, b.p. $148\text{--}150^\circ/17$ mm. (dibromide, m.p. 153°), oxidised (perphthalic acid) to α -cyclohexyl- β -phenylethylene oxide (III), b.p. $158\text{--}160^\circ/15$ mm. When (III) is heated with $MgBr_2$ etherate it gives cyclohexyl benzyl ketone (IV) (50—60%), m.p. 26° , b.p. $163\text{--}165^\circ/15$ mm. (semicarbazone, m.p. 142°). $CH_2Ph\cdot CHO$ with Mg cyclohexyl chloride gives α -cyclohexyl- β -phenylethyl alcohol, m.p. 57° , b.p. $167\text{--}168^\circ$ (p-nitrobenzoate, m.p. 18°), oxidised (CrO_3) to (IV). J. L. D.

Hydrogenation of acetylenic compounds. XXXI. Catalytic hydrogenation of acetylenic γ -glycols with a cyclopentyl radical. J. S. SALKIND and I. M. GVERDTZITELI (J. Gen. Chem. Russ., 1939, 9, 855—862).—cyclopentanone and $(\text{C}\cdot MgBr)_2$ yield $\alpha\beta$ -di-(1-hydroxycyclopentyl)acetylene, m.p. $109\text{--}8\text{--}110\text{--}8^\circ$ (diacetate, m.p. $44\text{--}5\text{--}45\text{--}5^\circ$), hydrogenated (Pd on starch) to isomeric ethylenic glycols, m.p. $82\text{--}83^\circ$ and $129\text{--}6\text{--}130\text{--}6^\circ$, converted by dil. H_2SO_4 into the γ -oxide, m.p. $81\text{--}82^\circ$, and completely hydrogenated (Pt-black) to $\alpha\beta$ -di-(1-hydroxycyclopentyl)ethane, m.p. $131\text{--}2\text{--}132\text{--}4^\circ$. γ -Hydroxy- α -(1-hydroxycyclopentyl)- γ -methyl- Δ^2 -butinene, m.p. $56\text{--}58^\circ$, b.p. $125\text{--}126^\circ/6$ mm., synthesised from $MgEtBr$, $CH_3\text{C}\cdot CMe_2\cdot OH$, and cyclopentanone, is hydrogenated (Pd) to the H_2 -derivative, m.p. $89\text{--}90^\circ$. It is concluded that the rates of hydrogenation of di-tert.-acetylenic glycols are influenced by steric hindrance and by the mol. wts. and vols. of the substituents.

V. A. P.

Behaviour of cis- and trans-isomerides in the dehydration of 1-methylcyclopentane-1:2-diols and dehalogenation of the corresponding halogenohydrins. M. TIFFENEAU and G. VAISSIÈRE (Compt. rend., 1939, 209, 449—453; cf. A., 1935, 340; 1938, II, 97).—2-Chlorocyclopentanone (I) with $MgMeBr$ affords cis-2-chloro-1-methylcyclopentanol (II), the $\text{O}\cdot MgBr$ derivative (prep. by $MgEtBr$) of which when heated gives (after hydrolysis) 2-methylcyclopentanone (III) (semicarbazone, m.p. 184°) by a semipinacolic change. 1-Methyl- Δ^1 -cyclopentene with $NH_2\cdot CO\cdot NHCl$ in aq. AcOH gives trans-(II), similarly converted into (III). (I) with boiling H_2O (+ $BaCO_3$) affords a ketol converted by $MgMeBr$ into cis-1-methylcyclopentane-1:2-diol (IV), b.p. $105^\circ/15$ mm., m.p. 23° , dehydrated by hot 10% H_2SO_4 to (III). trans-(IV) with hot dil. H_2SO_4 gives only resins but the

vapour passed over Al_2O_3 at $300^\circ/20$ mm. gives unsaturated hydrocarbons and their polymerides and a small amount of (III). J. L. D.

Triarylcarbinols. VII. **Diphenyl-4'-dimethylaminodiphenylcarbinol and its relation to the theory of colour of dyes.** A. A. MORTON and W. H. WOOD. VIII. **Occurrence of colour with triphenylcarbonium salts.** A. A. MORTON and L. F. MCKENNEY (J. Amer. Chem. Soc., 1939, 61, 2902—2905, 2905—2908; cf. A., 1938, II, 137).—VII. *Diphenyl-4'-dimethylamino-p-diphenylcarbinol*, m.p. $177\text{--}178^\circ$ [prep. from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{-}p$ (I), COPh_2 , and Na in boiling C_6H_6], gives no colour with dil. acids; the NMe_2 is more basic than the $\geq\text{C}\cdot\text{OH}$, and halochromism is not observed until after neutralisation of the NMe_2 . This does not accord with the carbenium theory of CHAr_3 dyes. The following orders of basicity are established: $(p\text{-C}_6\text{H}_4\text{Ph})_3\text{C}\cdot\text{OH} > \text{NH}_2\text{Ac}$, $\text{NH}_2\text{Bz} > \text{CPh}_3\cdot\text{OH}$; $m\text{-} \gg o\text{-}$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. The yield of (I) from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{-}p$, MeOH , and conc. HCl at $140\text{--}150^\circ$ is much greater in a short than in a long tube.

VIII. *Triphenylcarbonium perchlorate* (I), m.p. $219\cdot5\text{--}220^\circ$, and sulphate (impure), $(\text{C}_6\text{H}_4\text{Ph})_3\text{CX}\cdot\text{HX}$, are prepared by adding HX to $(\text{C}_6\text{H}_4\text{Ph})_3\text{C}\cdot\text{OH}$ (II) in Ac_2O . The nitrate is prepared by HNO_3 (d 1·6). Salts of weaker acids could not be obtained, but HCl produces a colour with (II) in AcOH if a trace of H_2O , MeNO_2 , MeCN , $\text{HCO}\cdot\text{NH}_2$, $\text{CO}(\text{NH}_2)_2$, MeOH , NH_2Bz , etc. is present. HNO_3 gives a colour in AcOH in presence of a little MeNO_2 . Electrolysis of (I) in org. solvents causes disappearance of colour at the cathode; with a very dil. solution of (I) in PhNO_2 there is appearance of colour at the anode. With (I) in MeNO_2 the bulk of the (II) is recovered from the cathode compartment. $\text{CPh}_3\cdot\text{ClO}_4$ behaves similarly. Colour is thus dependent on presence of ClO_4^- . With crystal-violet, however, colour follows the ammonium ion. R. S. C.

Saponins and sapogenins. XIII. **Precipitability of steroid sapogenins by digitonin.** C. R. NOLLER (J. Amer. Chem. Soc., 1939, 61, 2717—2719; cf. A., 1939, II, 517).—The solubility products of digitonides of steroid sapogenins, all $>$ those of cholesterol and β -cholestanol digitonides, have configurational val. only when epimeric pairs are compared. Behaviour under arbitrary conditions is misleading. R. S. C.

Steroids and sex hormones. LVIII. **Transformation of 17-acetylenylandrosterone-3 : 17-diol into pregnadien-3-ol.** L. RUZICKA, M. W. GOLDBERG, and E. HARDEGGER (Helv. Chim. Acta, 1939, 22, 1294—1300).—Gradual addition of a solution of Δ^5 -17-acetylenylandrosterone-3 : 17-diol in abs. EtOH to a suspension of Na in boiling xylene and treatment of the product with $\text{Ac}_2\text{O}\text{-C}_5\text{H}_5\text{N}$ gives *pregnadien-3-ol acetate*, m.p. $143\text{--}144^\circ$, $[\alpha]_D -70\cdot3 \pm 0\cdot3^\circ$ in CHCl_3 , hydrolysed ($\text{KOH}\text{-MeOH}$) to *pregnadien-3-ol* (I), m.p. $132\text{--}133^\circ$, $[\alpha]_D -74 \pm 1^\circ$ in CHCl_3 . This is oxidised $[\text{Al}(\text{O}i\text{Bu})_3\text{-C}_6\text{H}_6\text{-COMe}_2]$ to *pregnadien-3-one*, m.p. $142\text{--}143^\circ$, $[\alpha]_D +117\cdot5 \pm 1^\circ$ in CHCl_3 . (I) is hydrogenated (PtO_2 in $\text{EtOH}\text{-AcOH}$) to *allopregnan-3-ol*, m.p. $137\text{--}138^\circ$, $[\alpha]_D +16 \pm 1^\circ$ in CHCl_3 (acetate,

m.p. $115\text{--}116^\circ$), which is oxidised (CrO_3 in AcOH) to *allopregnan-3-one*, m.p. $116\text{--}117^\circ$ [*semicarbazone*, m.p. $\sim 230^\circ$ (decomp.)]. The corresponding *hydrazone*, m.p. $\sim 226^\circ$ (decomp.), is transformed by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and NaOEt in EtOH at 200° into *allopregnane*, m.p. $84\text{--}85^\circ$, $[\alpha]_D +18\cdot0 \pm 0\cdot7^\circ$ in CHCl_3 . M.p. are corr. H. W.

Stigmasterol 22 : 23-dibromide. E. FERNHOLZ and H. E. STAVELY (J. Amer. Chem. Soc., 1939, 61, 2956—2957).—Stigmasteryl acetate tetrabromide and NaI in $\text{C}_6\text{H}_6\text{-EtOH}$ at room temp. (not when heated) give the *acetate 22 : 23-dibromide* (60%), m.p. $212\text{--}213^\circ$, $[\alpha]_D^{25} +30^\circ$ in CHCl_3 , hydrolysed by hot 5% $\text{KOH}\text{-MeOH}$ to *stigmasterol 22 : 23-dibromide*, m.p. $209\text{--}210^\circ$, which with $\text{Al}(\text{O}i\text{Bu})_3$ in $\text{C}_6\text{H}_6\text{-COMe}_2$ gives *stigmastadienone 22 : 23-dibromide*, m.p. $182\text{--}184^\circ$, $[\alpha]_D^{25} +53^\circ$ in CHCl_3 , and thence ($\text{Zn dust}\text{-AcOH}$; 100°) *stigmastadienone*, m.p. $124\text{--}125^\circ$, $[\alpha]_D^{25} +63^\circ$ in CHCl_3 , also obtained from stigmasterol by $\text{Al}(\text{OPr}^i)_3$ in *cyclohexanone-PhMe*. R. S. C.

Introduction of nitrogen into sterols. III. **Preparation of deoxycholamine.** M. VANGHELOVICI (Bul. Soc. Chim. România, 1938, 20, 231—235; cf. A., 1938, II, 405).—Deoxycholhydrazide (modified prep. from the acid by way of the Et ester) gives the azide, decomp. $\sim 67^\circ$, and thence the *urethane*, m.p. 110° , which, when distilled with CaO at 4 mm., gives *deoxycholamine*, m.p. 118° [*hydrochloride*, m.p. 247° (decomp.)]; *platinichloride*, decomp. 194° . R. S. C.

Action of sulphur monochloride on phenyl-acetonitrile. V. V. KORSCHAK and A. F. LISSEENKO (J. Gen. Chem. Russ., 1939, 9, 1329—1331).— $\text{CH}_2\text{Ph}\cdot\text{CN}$ and S_2Cl_2 in the cold yield $\text{CHClPh}\cdot\text{CN}$ (I), $\text{CCl}_2\text{Ph}\cdot\text{CN}$ (II) and $(\text{CPh}\cdot\text{CN})_2$ (III); on heating (I) is no longer formed and the principal product is *s-dichlorodiphenylsuccinodinitrile*, m.p. $189\text{--}190^\circ$, hydrolysed by $\text{KOH}\text{-EtOH}$ to $\alpha\beta$ -diphenylmaleic anhydride and converted into (III) by heating. G. A. R. K.

Stereochemical studies. XX. **Optically active phenylethylthiolacetic acids and phenylethyl mercaptans.** B. HOLMBERG (Arkiv Kemi, Min., Geol., 1939, 13, A, No. 8, 9 pp.).—*r*- α -Phenylethylthiolacetic acid (I) is resolved by α -phenylethylamine in H_2O . The non-cryst. (—)-acid (II), $[\alpha]_D -333\cdot2^\circ$ in abs. EtOH , -234° in H_2O , -208° in 0·1N-HCl [(—)-phenylethylamine, m.p. $124\text{--}125^\circ$, $[\alpha]_D -180\cdot8^\circ$ in abs. EtOH , and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. $76\text{--}77^\circ$, $[\alpha]_D -193\cdot5^\circ$ in abs. EtOH , salts], and the (+)-acid (III) [(+)-phenylethylamine, m.p. $124\text{--}125^\circ$, $[\alpha]_D +180\cdot7^\circ$ in abs. EtOH , and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. $76\text{--}77^\circ$, $[\alpha]_D +191\cdot7^\circ$ in abs. EtOH , salts] are described. (I) gives cryst. salts, m.p. $53\text{--}55^\circ$, $56\text{--}57\cdot5^\circ$, $65\text{--}66^\circ$, and $105\text{--}106^\circ$, respectively, with NH_2Ph , *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, and $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$, whereas that with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ is non-cryst. With benzenoid bases (II) and (III) yield non-cryst. salts. Slight racemisation is observed when (II) or (III) is heated in neutral and possibly in alkaline aq. solution but not in 0·1N-HCl. (II) is oxidised by KSO_4 to the sulphinacetic acid, m.p. $126\text{--}127^\circ$ (decomp.), $[\alpha]_D -120\cdot2^\circ$ in abs. EtOH , which is converted by H_2SO_4 into (—)- α -phenylethyl mercaptan (IV), b.p.

82—83°/10 mm., $[\alpha]_D^{25} -105.6^\circ$, $[\alpha]_D -89.0^\circ$ in abs. EtOH. Oxidation of (III) with H_2O_2 gives an acid, m.p. 126—127° (decomp.), $[\alpha]_D +142.0^\circ$ in abs. EtOH, which gives (+)- α -phenylethyl mercaptan (V), b.p. 81—83°/10 mm., $[\alpha]_D^{25} +105.8^\circ$. Oxidation (EtOH-I) of (V) and (IV) gives (+)- (VI) and (—)-*di*- α -phenylethyl disulphide, $[\alpha]_D +271.9^\circ$ and -272.1° in abs. EtOH, respectively. Prolonged treatment of (V) with H_2O_2 yields (VI) and α -phenylethanesulphonic acid (Na, $[\alpha]_D +4.7^\circ$ in H_2O , and β - $C_{10}H_7 \cdot NH_2$ salt, m.p. 196—197° after darkening, $[\alpha]_D +9.5^\circ$ in abs. EtOH).

H. W.

3 : 5-Di-iodo-*l*-tyrosine, its properties and preparation. A. J. SAVITZKI (J. Gen. Chem. Russ., 1939, 9, 1342—1344).—*l*-Tyrosine in aq. NH_3 affords with I in KI at 6—8° >80% of crude di-iodotyrosine, which is purified by reprecipitation from HCl; the yield of pure product, m.p. 200—203°, is ~72%. It has 2 H_2O of crystallisation, which it loses on prolonged drying over H_2SO_4 . The *dl*-compound retains 1 H_2O under the same conditions and is therefore a true racemate, not a mixture of the two forms.

G. A. R. K.

α -Benzoyl-, m.p. 200—202°, $[\alpha]_D +3.3^\circ$ in H_2O (2.8%), and α -hippuryl-*l*-lysine amide hydrochlorides, m.p. 255—258°, $[\alpha]_D^{25} -11.7^\circ$ in H_2O (5%); ϵ -carbobenzoyloxy- α -hippuryl-lysine, m.p. 148—149°.—See A., 1939, III, 1009.

Hydrolysis of benzoic and related esters in varying media.—See A., 1939, I, 615.

Interaction of sulphuryl chloride with aryl-amides of aromatic acids. II. Orienting influences of groups in substitution reactions in aromatic compounds. N. W. HIRWE, G. V. JADHAV, and D. R. SUKHTANKAR (J. Indian Chem. Soc., 1939, 16, 281—284; cf. A., 1939, II, 263).—Salicyl-anilide and -*o*-, -*m*-, and -*p*-toluidide and SO_2Cl_2 in boiling C_6H_6 give respectively 5-chlorosalicyl-anilide, m.p. 203—204°, and 4'-chloroanilide, m.p. 215—216°, and 3 : 5-dichlorosalicyl-2' : 4'-dichloroanilide, m.p. 174—175°; 5-chloro-, m.p. 171—172°, and 3 : 5-dichloro-salicyl-5'-chloro-*o*'-toluidide, m.p. 197—198°; 5-chlorosalicyl-*m*'-toluidide, m.p. 144—145°, and 6'-chloro-*m*'-toluidide, m.p. 221—222°, and 3 : 5-dichlorosalicyl-4' : 6'-dichloro-*m*'-toluidide, m.p. 214—215°; and 5-chlorosalicyl-*p*'-toluidide, m.p. 216—217°, and 3 : 5-dichlorosalicyl-3'-chloro-*p*'-toluidide. *o*-Methoxybenz-anilide and -*o*'-anisidide give *o*-methoxybenz-*p*'-chloroanilide, m.p. 75—76°, and 5'-chloro-*o*'-anisidide, m.p. 135—136°. *o*-Tolu-anilide and -*o*'-, -*m*'-, and -*p*'-toluidide give respectively *o*-tolu-*p*'-chloroanilide, m.p. 133—134°, and 2' : 4'-dichloroanilide, m.p. 128°, 5'-chloro-*o*'-toluidide, m.p. 182°, 4' : 6'-dichloro-*m*'-toluidide, m.p. 120—121°, and 3'-chloro-*p*'-toluidide, m.p. 119—120°. *o*-Chlorobenz-anilide and -*m*'-chloroanilide give *o*-chlorobenz-*p*'-chloro-, m.p. 119—120°, and 3' : 4'-dichloro-anilide, m.p. 143°. The structures of the products are proved by hydrolysis to known amines and acids, and in three cases by synthesis.

E. W. W.

Stereochemistry of diphenyls. XLVIII. Comparison of the racemisation rates of three isomeric 2 : 2' : 6-nitrocarboxymethyldiphenyls. R.

ADAMS and J. B. HALE. XLIX. Comparison of the racemisation rates of the 2 : 2' : 6-nitrocarboxymethoxydiphenyls. R. ADAMS and G. C. FINGER (J. Amer. Chem. Soc., 1939, 61, 2825—2828, 2828—2830; cf. A., 1939, II, 505).—XLVIII. 3 : 2 : 1- $NO_2 \cdot C_6H_3Br \cdot CO_2Me$, *o*- C_6H_4MeI , and Cu powder at 225—230° give an ester, hydrolysed to 6-nitro-2'-methyldiphenyl-2-carboxylic acid (15%), m.p. 162—163°, resolved to the *l*-, m.p. 153—155°, $[\alpha]_D^{25} -65^\circ$ in EtOH [quinine salt (+ xH_2O), m.p. 135—140° and (anhyd.) m.p. 168—171°, $[\alpha]_D^{25} -133.5^\circ$ in $CHCl_3$], and *d*-acid (I), m.p. 153—156°, $[\alpha]_D^{25} +61.5^\circ$ in EtOH [quinine salt, m.p. (+ xH_2O) 118—123° and (anhyd.) 128—131°, $[\alpha]_D^{25} (+xH_2O) -105^\circ$ in $CHCl_3$]. 3 : 2 : 1- $C_6H_3MeI \cdot CO_2Me$, *o*- $C_6H_4I \cdot NO_2$, and Cu powder at 230° (later 250°) give 2'-nitro-2-methyldiphenyl-6-carboxylic acid (50%), m.p. 157°, resolved by brucine in MeOH into the *d*-, m.p. 179—181°, $[\alpha]_D^{25} +73.5^\circ$ in $CHCl_3$ (*brucine* salt, m.p. 165—167°, $[\alpha]_D^{25} +48^\circ$ in $CHCl_3$), and *l*-acid (II), m.p. 175—179°, $[\alpha]_D^{25} -72.6^\circ$ in $CHCl_3$ (*brucine* salt, m.p. 153—160°, $[\alpha]_D^{25} -51^\circ$ in $CHCl_3$). *d*- and *l*-6-Nitrodiphenic acid (III) are prepared having $[\alpha]_D^{25} +39.0^\circ$ and -37.5° in EtOH. 3 : 2 : 1- $NO_2 \cdot C_6H_3Br \cdot CO_2Me$, *o*- $C_6H_4I \cdot NO_2$, and Cu-bronze at 220—225° give 2 : 2'-dinitrodiphenyl-6-carboxylic acid (30%), m.p. 164°, resolved by quinine in 75% EtOH into the *d*-, m.p. 135—137°, $[\alpha] +201.5^\circ$ in EtOH (*quinine* salt, m.p. 195—197°, $[\alpha]_D^{25} +52.5^\circ$ in $CHCl_3$), and *l*-acid (IV), m.p. 127—130°, $[\alpha]_D^{25} -199.5^\circ$ in EtOH (*quinine* salt, m.p. 121—125°, $[\alpha]_D^{25} -238^\circ$ in $CHCl_3$). $[\alpha]$ are given for the acids also in other solvents. Relative stability against racemisation is 2-nitro-6-methyldiphenyl-2'-carboxylic acid > (II) > (I), which does not accord with theory. (III) is more stable than (IV) in Bu^oOH , but less stable in $AcOH$ or aq. $NaOH$.

XLIX. 1 : 2 : 3- $OMe \cdot C_6H_3I \cdot CO_2Me$, *o*- $C_6H_4I \cdot NO_2$, and Cu-bronze at 200° give 2'-nitro-2-methoxydiphenyl-6-carboxylic acid, m.p. 234—236°, which affords the *l*-acid (V), m.p. 229—232°, $[\alpha]_D^{25} -213.3^\circ$ in EtOH (*brucine* salt, m.p. 222—225°, $[\alpha]_D^{25} -47.1^\circ$ in $CHCl_3$). 1 : 2 : 3- $OMe \cdot C_6H_3Cl \cdot NO_2$ (prep. described), *o*- $C_6H_4I \cdot CO_2Me$, and Cu-bronze at 255—280° give 6-nitro-2-methoxydiphenyl-2'-carboxylic acid, m.p. 196—198° (and 6 : 6'-dinitro-2 : 2'-dimethoxydiphenyl, m.p. 226—228°), resolved by brucine in abs. EtOH into the *l*-acid (VI), m.p. 195—199°, $[\alpha]_D^{25} -127.9^\circ$ in abs. EtOH (*brucine* salt, m.p. variable, $[\alpha] \sim 0$). Half-life periods of (V) and (VI) in abs. EtOH are 271 and 219—288 min., respectively, but that of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid, $[\alpha]_D^{25} +59.4^\circ$ in abs. EtOH, is only 10.2 min.

R. S. C.

Naphthenic acids (from Grosny petroleum). I. I. I. LAPKIN (J. Gen. Chem. Russ., 1939, 9, 1332—1341).—Fractionation and analysis of the Me esters of naphthenic acids suggest that they contain from 10 to 18 C; C_{10} and C_{11} are monocyclic, C_{12} and C_{13} mono- and di-cyclic, and above C_{14} dicyclic only; no tri- or poly-cyclic acids were detected. No appreciable amounts of aliphatic acids can be present in the original mixture, judging from the max. crit. solution temp. in NH_2Ph , of the hydrocarbons prepared by reducing the esters to the alcohols, conversion into the iodides, and reduction with Zn dust.

The parachors of the esters below C_{13} point to the presence of 5- and 6-membered rings. The rate of esterification of the acids is in agreement with the primary character of the CO_2H group. G. A. R. K.

Cyclisation of benzylbenzylidenesuccinic acid. E. BERGMANN and A. WEIZMANN (Compt. rend., 1939, 209, 539—540; cf. A., 1938, II, 415; Dufraisse and Houpillart, A., 1938, II, 194).—Interaction of Me benzylsuccinate and PhCHO gives a product (I) which when distilled in a vac. is converted into 1-hydroxy-2-benzyl-3-naphthoic acid, b.p. 184—188°/0.02 mm., m.p. 65—68°. (I) with AcOH gives α -benzyl- α' -benzylidenesuccinic acid, converted by conc. H_2SO_4 at 70°/1 hr. into 1:5-diketo-2:3:6:7-dibenzo-1:4:5:10-tetrahydronaphthalene, m.p. 265°, which with a large excess of LiPh gives 6-hydroxy-12-phenylnaphthacene, m.p. 255°. J. L. D.

Alkyl hydrogen phthalates from normal aliphatic alcohols. J. F. GOGGANS, jun., and J. E. COPENHAVER (J. Amer. Chem. Soc., 1939, 61, 2909—2910).—Heating ROH with o - $C_6H_4(CO_2O)$ under reflux ($R = Me$ to Bu) or, in other cases, at 105—110° gives Me, m.p. 82.4—82.7°, Et, *Pr*, m.p. 54.1—54.4°, *Bu*, m.p. 73.1—73.5°, *amyl*, m.p. 75.4—75.6°, *hexyl*, m.p. 24.6—25.4°, C_7H_{15} , m.p. 16.5—17.5°, C_8H_{17} , m.p. 21.5—22.5°, C_9H_{19} , m.p. 42.4—42.6°, $C_{10}H_{21}$, m.p. 37.8—38.0°, $C_{11}H_{23}$, m.p. 43.8—44.1°, $C_{12}H_{25}$, m.p. 50.2—50.4°, $C_{13}H_{27}$, m.p. 52.4—52.7°, $C_{14}H_{29}$, m.p. 59.8—60.0°, $C_{15}H_{31}$, m.p. 60.3—60.5°, $C_{16}H_{33}$, new m.p. 66.7—66.9°, $C_{17}H_{35}$, m.p. 66.6—66.8°, $C_{18}H_{37}$, m.p. 72.4—72.6°, $C_{19}H_{39}$, m.p. 70.8—71.0°, and $C_{20}H_{41}$, m.p. 77.1—77.3°, *H phthalate*. All alkyl are *n*. M.p. are corr. R. S. C.

Reaction of the Grignard reagent with homophthalic anhydride. C. C. PRICE, F. M. LEWIS, and M. MEISTER (J. Amer. Chem. Soc., 1939, 61, 2760—2762).—Under all conditions, homophthalic anhydride (I) and $MgMeI$ give dimethylhomophthalide. (I) is readily prepared from o - $C_6H_4Me \cdot CO_2H$ by way of o - $C_6H_4Me \cdot COCl$, o - $CH_2Br \cdot C_6H_4 \cdot COBr$, o - $CH_2Br \cdot C_6H_4 \cdot CO_2Et$, o - $CN \cdot CH_2 \cdot C_6H_4 \cdot CO_2Et$, and o - $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (by 50% H_2SO_4 at 100°) in 70—75% over-all yield. Phthalide and KCN at 180—190° give 80—85% of o - $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CN$. R. S. C.

Friedel and Crafts reactions affected by steric hindrance. B. Hoi (Compt. rend., 1939, 209, 562—564; cf. A., 1939, II, 429).—When phthalonic or homophthalic anhydride is submitted to the Friedel-Crafts reaction or to esterification, the incoming group is always separated from the ring by 2 C because of steric effects. J. L. D.

Steroids and sex hormones. LV. Preparation of $\Delta^{5:17}$ -3-hydroxypregnadiene-21-carboxylic acid and its hydrogenation products. P. A. PLATTNER and W. SCHRECK (Helv. Chim. Acta, 1939, 22, 1178—1184).— Δ^5 -3:17-Dihydroxyandrostene-17-acetic acid yields a *Me* ester, m.p. 159°, $[\alpha]_D -89 \pm 2^\circ$ in $CHCl_3$ (3-acetate, m.p. 117°, $[\alpha]_D -68 \pm 2^\circ$ in $CHCl_3$), the diacetate, two forms, m.p. 113° and 121°, $[\alpha]_D -70 \pm 2^\circ$ in $CHCl_3$, of which is converted by distillation under 15 mm. into *Me* $\Delta^{5:17}$ -3-acetoxypregnadiene-21-carboxylate (I), m.p.

159°, $[\alpha]_D -69 \pm 2^\circ$ in $CHCl_3$, hydrolysed by KOH - $MeOH$ to $\Delta^{5:17}$ -3-hydroxypregnadiene-21-carboxylic acid, m.p. 249—250°, $[\alpha]_D -82 \pm 1^\circ$ in dioxan [*Me* ester (II), m.p. 188—189°, $[\alpha]_D -73 \pm 1^\circ$ in dioxan]. (II) in $COMe_2$ is oxidised by $Al(OBu)_3$ in C_6H_6 to *Me* $\Delta^{4:17}$ -3-ketopregnadiene-21-carboxylate, m.p. 151—152°, $[\alpha]_D +80 \pm 1^\circ$ in dioxan. Hydrogenation (PtO_2 in $EtOH$) of (I) affords *Me* Δ^5 -3-acetoxypregnene-21-carboxylate, m.p. 128—129°, $[\alpha]_D 57 \pm 1^\circ$ in $CHCl_3$, which is hydrolysed (KOH - $MeOH$) to Δ^5 -3-hydroxypregnene-21-carboxylic acid, m.p. 241—242°, $[\alpha]_D -56.4 \pm 1^\circ$ in dioxan, converted by CH_2N_2 into the *Me* ester (III), m.p. 132—133°, $[\alpha]_D -63.5 \pm 1^\circ$ in dioxan. Oxidation [$Al(OBu)_3$ in C_6H_6 - $COMe_2$] of (III) affords *Me* Δ^4 -3-ketopregnene-21-carboxylate, m.p. 146—147°, $[\alpha]_D +84 \pm 1^\circ$ in dioxan. (I) is hydrogenated (Pt in $AcOH$) to *Me* 3-acetoxyallopregnane-21-carboxylate, m.p. 150—151°, $[\alpha]_D 0 \pm 1^\circ$ in dioxan. All m.p. are corr. H. W.

Introduction of nitrogen into the sterol molecule. IV. Condensation of bile acid hydrazides with carbonyl compounds. M. VANGHELOVICI (Bul. Soc. Chim. România, 1938, 20, 237—241).—Cholhydrazide and $RCHO$ in dil. HCl give the *CHPh*·, m.p. 148°, *p*- $OMe \cdot C_6H_4 \cdot CH$ ·, m.p. 140°, *salicylidene*, m.p. 160°, *CHPh*· $CH \cdot CH$ ·, m.p. 150°, *furfurylidene*, m.p. 145°, CH_2 ·, m.p. 210°, and $CO_2Et \cdot CH_2 \cdot CMe$ ·, m.p. 210° (could not be cyclised), derivatives. Deoxycholhydrazide gives the CH_2 ·, m.p. 214° (decomp.), *furfurylidene*, m.p. 136°, *p*- $OMe \cdot C_6H_4 \cdot CH$ ·, m.p. 167°, and *CHPh*· derivative, m.p. 75°. Cholanhydrazide gives CH_2 ·, m.p. 130°, and *CHPh*· derivatives, m.p. 146°. Other alkylidene derivatives could not be obtained. R. S. C.

Sterols. LXXII. Oxidation products of sarsapogenin. C_{19} -Dibasic acid. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 2722—2724).—(?) 3-Hydroxy α -tibilianic acid (I), m.p. 220—222° [*Me*· ester, m.p. 121—122° (acetate, m.p. 103—104°); acetate anhydride, m.p. 203—204°, hydrolysed to (I) by KOH - $EtOH$], is obtained by CrO_3 from sarsapogenin acetate at 85° (cf. A., 1939, II, 322), sarsapogeninic acid acetate (12% yield) at 90—95°, or tetrahydrosarsapogenin acetate at 90—95°. CrO_3 - $AcOH$ at room temp., followed by hot Zn - Hg - HCl , converts (I) into (?) α -tibilianic acid, m.p. 230—232° (anhydride, m.p. 205.5—207°). R. S. C.

Degradation of α -diphenyloctatetraene to ζ -phenylheptatrienal. P. KARRER and H. OBST (Helv. Chim. Acta, 1939, 22, 1191—1192).— α -Diphenyloctatetraene in $CHCl_3$ is oxidised by acid $KMnO_4$ to trans-trans-trans- ζ -phenylheptatrienal, m.p. 112.5—113° [*oxime*, m.p. 186—187° (decomp.)]. H. W.

Polyene series. I. E. BARRACLOUGH, J. W. BATTY, I. M. HEILBRON, and W. E. JONES. II. I. M. HEILBRON, W. E. JONES, and A. SPINKS. III. J. W. BATTY, I. M. HEILBRON, and W. E. JONES. IV. I. M. HEILBRON, A. W. JOHNSON, and W. E. JONES (J.C.S., 1939, 1549—1554, 1554—1556, 1556—1560, 1560—1563).—I. Data in brackets refer to max. of absorption spectra. Citral, $CHMe \cdot CH \cdot CHO$, piperidine, and $AcOH$ (excess) give (cf. A., 1937, II,

342) citrylideneacetaldehyde- α (I) [3140 A.; ϵ 12,490] (semicarbazone, m.p. 160° [3255 A.; ϵ 27,100]) and less - β (II) [3160 A.; ϵ 12,800] (semicarbazone, m.p. 206° [3255 A.; ϵ 24,400]), yields of both products being increased by addition of SiO₂ gel; use of piperidine acetate and SiO₂ gel gives somewhat larger amounts; use of NaNH₂ in Et₂O leads to (I) [no (II)] and a cyclic aldehyde (III), C₁₄H₂₀O (*semicarbazone*, m.p. 186° [2860 A.; ϵ 50,000], absorbs 4 H₂). Citral, MeCHO, and NaNH₂ in Et₂O give citrylideneacetaldehyde (semicarbazone, m.p. 166—168° [3045 A.; ϵ 49,000]), and a little (III). Al(OPr^{*i*})₃-Pr^{*i*}OH reduces (I) and (II) to η -*dimethyl- $\Delta^{\beta\gamma}$ -dodecatrien- α -ol*, b.p. 200—210°/30 mm. [2680 A.; ϵ 12,000] (absorbs 4 H₂), and an alcohol [2650 A.; ϵ 10,000], respectively. Citral, CMe₂:CH:CHO, and NaNH₂ in Et₂O give ψ -ionylideneacetaldehyde- α (IV) [3150 A.; ϵ 14,700] (*semicarbazone*, m.p. 178—179° [3250 A.; ϵ 33,000], absorbs 5 H₂) and - β (V) [3150 A.; ϵ 11,000] (*semicarbazone*, m.p. 112° [3240 A.; ϵ 24,000]), reduced to alcohols [2650 and 2660 A.; ϵ 11,000 and 10,000, respectively]. O₃ yields 0.77 mol. of COMe₂ from (I) and 0.70 mol. from (IV), but no MeCHO from either. CHPh:CH:CHO, MeCHO, and NaNH₂-Et₂O give CHPh:CH:CH:CHO (semicarbazone, m.p. 218—218.5° [3390 A.; ϵ 52,460]). COMe₂, (I), and NaOEt-EtOH at 0° give κ -*dimethyl- $\Delta^{\gamma\eta}$ -pentadecapentaen- β -one*, b.p. 140—145°/1 mm. [3580 A.; ϵ 14,500] (*semicarbazone*, m.p. 171° [3500 A.; ϵ 15,750]); (IV) gives similarly ζ -*trimethyl- $\Delta^{\gamma\eta}$ -pentadecapentaen- β -one*, b.p. 164°/0.5 mm. [3580 A.; ϵ 15,400] (*semicarbazone*, m.p. 161° [3500 A.; ϵ 15,000]).

II. The semicarbazone [2995 A.; ϵ 45,400] of ψ -ionone [2910 A.; ϵ 21,800] and H₃PO₄ (d 1.75) at room temp. give after subsequent hydrolysis) nearly pure β -ionone [2935 A.; ϵ 9,200] (semicarbazone [2765 A.; ϵ 23,300]), but ψ -ionone itself gives mainly α -ionone [2285 A.; ϵ 14,300]. The semicarbazone [3045 A.; ϵ 47,200] of citrylideneacetaldehyde [2900 A.; ϵ 15,960] gives similarly β -*cyclocitrylideneacetaldehyde* [β -2:6:6- Δ^1 -cyclohexenylacetaldehyde] [2930 A.; ϵ 8,000] (*semicarbazone*, m.p. 186—187° [2950 A.; ϵ 27,000]), yielding with O₃ geronic acid and with COMe₂-NaOEt-EtOH ζ -2:6:6- Δ^1 -cyclohexenyl- $\Delta^{\gamma\epsilon}$ -hexadien- β -one, b.p. 140—145°/0.17 mm. [3190 A.; ϵ 8280] (*semicarbazone*, m.p. 186° [3160 A.; ϵ 38,000]).

III. The semicarbazone of (I) and H₃PO₄ give (?) 5:5:9-*trimethyl-5:6:7:8:9:10-hexahydro-1-naphthaldehyde*, m.p. 60—61° [3210 A.; ϵ 13,260] (*semicarbazone*, +MeOH, m.p. 114° [3230 A.; ϵ 28,000]; 2:4-dinitrophenylhydrazone, m.p. 186°), reduced by Al(OPr^{*i*})₃-Pr^{*i*}OH to the corresponding alcohol [2680 A.; ϵ 10,000] (absorbs 3 H₂) and yielding with O₃ a keto-dicarboxylic acid, C₁₂H₁₈O₅ (*semicarbazone*, m.p. 163°), and no geronic acid. The semicarbazones of (II), (IV), and (V) yield similarly dicyclic aldehydes, m.p. 56.5—60.5° [2350 A.; ϵ 14,000] (*semicarbazone*, m.p. 221—222° [2680 A.; ϵ 33,300]; 2:4-dinitrophenylhydrazone, m.p. 253—254°; gives the derived alcohol, an oil, showing no selective ultra-violet absorption), an oil [3160 A.; ϵ 10,900] (*semicarbazone*, m.p. 189° [3250 A.; ϵ 24,000]; derived alcohol, an oil [2720 A.; ϵ 9,000];

with O₃ gives no geronic acid), and an oil [2400 A.; ϵ 8000] (*semicarbazone*, m.p. 214—215° [2670 A.; ϵ 27,500]).

IV. Vitamin-A, Al(OPr^{*i*})₃, and COMe₂ in boiling C₆H₆ give the same ketone, now termed axerophthylideneacetone (VI), as is obtained by Al(OBu^{*t*})₃-COMe₂ (A., 1938, II, 126). Al(OPr^{*i*})₃-Pr^{*i*}OH reduces this to the corresponding alcohol [3545 A.; ϵ 1_{cm}¹ 1250] [which, as also does (VI), gives geronic acid with O₃], but once a hydrocarbon [3700, 3900, and 4110 A.] was obtained. CHPh:CH:CH₂:OH with Al(OBu^{*t*})₃-COPr^{*i*} in C₆H₆ gives 5% of CHPh:CH:CHO, but with Al(OBu^{*t*})₃-COEt₂ in C₆H₆ gives δ -phenyl- α -methyl- $\Delta^{\gamma\epsilon}$ -butadienyl Et ketone, m.p. 63° [3220 A.; ϵ 33,400] (2:4-dinitrophenylhydrazone, m.p. 232°). With Al(OBu^{*t*})₃-COEt₂ in C₆H₆, CH₂Ph:OH and 2-furfuryl alcohol give α -benzylidene-, b.p. 160°/20 mm. [2730 A.; ϵ 25,000] (semicarbazone, m.p. 187°), and α -2-furfurylidene-ethyl Et ketone, b.p. 135—140°/21 mm. (*semicarbazone*, m.p. 181° [3160 A.; ϵ 74,000]; 2:4-dinitrophenylhydrazone, m.p. 188°), respectively.

R. S. C.

Vapour-phase production of *o*-tolualdehyde and phthalic anhydride from *o*-xylene.—See B., 1939, 1098.

Acylation of aldioximes. II. Inversion of configuration in the preparation of carbanilino-aldioximes from phenylcarbimide and *syn*-aldioximes. A. E. RAINSFORD and C. R. HAUSER (J. Org. Chem., 1939, 4, 480—492).—Brady's conclusion that PhNCO is capable of converting certain *syn*-aldioximes (I) into carbanilino-derivatives of the *anti*-compounds is confirmed and an explanation based on the intermediate formation of an "inner" salt is described. Inversion does not occur when (I) are treated with PhNCO in the presence of certain *tert.* amines, thus supporting the hypothesis that there is no inversion of configuration during the prep. of acyl derivatives when the reaction is carried out in solution in the presence of a sufficiently strong base. Investigation has been made of the action of C₅H₅N and NH₂Bu^{*t*} on carbanilino-derivatives of *syn*-3:4-methylenedioxy-, *syn*- and *anti*-*m*-nitro-, *syn*- and *anti*-*p*-dimethylamino-benzaldoxime and on the α -naphthylcarbanilino-compounds of *syn*- and *anti*-3:4-methylenedioxy-, *syn*-*p*-methoxy-, *syn*-*p*-dimethylamino-, and *anti*-*m*-nitro-benzaldoxime.

Brady's conclusion that there is no inversion of configuration when (I) are treated with 1-C₁₀H₇:NCO has been confirmed. α -Naphthylcarbanilino-*syn*-aldioximes may be recovered unchanged from C₅H₅N but are decomposed by NH₂Bu^{*t*} to *syn*-aldioximes; the corresponding *anti*-isomerides give nitriles with C₅H₅N or NH₂Bu^{*t*}. Carbanilino-*syn*-3:4-methylenedioxybenzaldoxime, m.p. 127°, is new.

H. W.

Structure of barbatolic acid. E. E. SUOMINEN (Suomen Kem., 1939, 12, B, 26—28).—Prolonged extraction of *Alectoria implexa* with boiling Et₂O gives barbatolic acid (3%) (I), decomp. 205—206° (dioxime, decomp. 207—208°), which with CH₂N₂ in Et₂O-dioxan at -5° gives *Me barbatolate* (II), decomp. 193° (sinters at 190°), converted by AcOH at 140—145° (sealed tube)/15 hr. into 2:6:4:1-

(OH)₂C₆H₂Me·CHO (atranol) (III) and 2 : 6-dihydroxy-3-carboxy-4-hydroxymethylbenzaldehyde (barbatol-carboxylic acid) (IV), decomp. 243—244°, which indicates that the CO₂H of (I) is in the barbatol nucleus. (II) with HI (*d* 1.7)—AcOH-Zn dust at 70—100° (or H₂-Pd-C) gives a compound (V), C₁₉H₂₀O₈, decomp. 189—190° (sinters at 186°), as well as β-orcinol and Me β-orcinolcarboxylate, which indicates that (III) and (IV) are probably linked through the CH₂·OH of (IV). (V) with CH₂N₂ in Et₂O gives a product, hydrolysed (boiling 0.2N-EtOH-KOH) to rhizonic acid, its Me ether, and the lactone, m.p. 173.5°, of 2 : 6-dimethoxy-4-hydroxymethyl-*m*-toluic acid (*Ag* salt). (I) is thus 3 : 5-dihydroxy-4-aldehydo-2-carboxybenzyl 3 : 5-dihydroxy-4-aldehydo-toluate. J. L. D.

cycloHexane series. II. Synthesis of ketones. G. VASILIU and S. RADVAN (Bul. Soc. Chim. România, 1938, 20, 243—250; cf. A., 1938, II, 408).—*cyclo*-Hexylphenylacetone (I) and 4 mols. of certain Grignard reagents give moderate yields of the ketones by way of the imine hydrohalides, but α-cyclohexyl-α-phenylpropionitrile (prep. from CHPhMe·CN by cyclohexyl bromide and NaNH₂ in Et₂O), b.p. 166°/11 mm., and C₆H₁₁·CPhR·CN (R = Et, Pr, or cyclohexyl) do not react in Et₂O, C₆H₆, or PhMe. Thus are obtained α-cyclohexylbenzyl Et (by MgEtBr in Et₂O), b.p. 163—164°/14 mm. [*semicarbazone*, m.p. 189°; *imine hydrobromide*, m.p. ~220° (decomp.)], Pr^α (by MgPr^αBr in Et₂O), b.p. 174°/13 mm. (*oxime*, m.p. 104°; *imine hydrobromide*, m.p. 193—194°), Pr^β (by MgPr^βBr in PhMe), m.p. 66—67° [*imine hydrobromide*, m.p. ~270° (decomp.)], and CH₂Ph ketone (by CH₂Ph·MgCl in PhMe), m.p. 74°, b.p. 219—220°/10 mm. Other CO-derivatives could not be obtained. MgMeI, MgBu^αBr, and Mg cyclohexyl bromide do not react with (I). MgPhBr and (I) in Et₂O give cyclohexyldeoxybenzoin, m.p. 121°. R. S. C.

Relative rates of reaction between ketones and liquid ammonia.—See A., 1939, I, 615.

Effect of nuclear and side-chain substitution on the oxonium-ion catalysed iodination of acetophenone derivatives. Kinetics of the iodination of acetophenone in sulphuric and perchloric acid solutions. Mechanism of the acid-catalysed enolisation of acetophenone derivatives.—See A., 1939, I, 617.

Isomerisation of cyclohexylphenylacetaldehyde. E. D. VENUS-DANILOVA and A. I. BOLSCHUCHIN (J. Gen. Chem. Russ., 1939, 9, 975—984).—α-cyclohexyl-β-phenylethyl alcohol (I) in AcOH and CrO₃ in H₂SO₄ at room temp. yield cyclohexyl benzyl ketone (II). β-cyclohexyl-α-phenylethyl alcohol (III) is oxidised similarly to Ph hexahydrobenzyl ketone (IV), b.p. 161—162°/10 mm. (*semicarbazone*, m.p. 192—193°; *oxime*, m.p. 99°). (II) when heated with KOH yields CH₂Ph·CO₂H and (I), whilst (IV) gives only (III) under these conditions. cyclohexylphenylacetaldehyde yields (I), together with a small amount of a *dimeride*, m.p. 150—151°, when treated with HgSO₄ in H₂SO₄ (6 hr. at 128—135°), or with H₂SO₄ at -5°. R. T.

Chalkones. I. Chalkones derived from resacetophenone and its dimethyl ether. J. B. LAL (J. Indian Chem. Soc., 1939, 16, 296—300).—2 : 4 : 1-(OMe)₂C₆H₃·COMe (I), isovanillin, MeOH, and 30% KOH-MeOH at 50—60° (24 hr.) give 2 : 4-dimethoxyphenyl 3'-hydroxy-4'-methoxystyryl ketone, m.p. 115°. With 6 : 2 : 1-, 3 : 2 : 1- (II); and 5 : 2 : 1-OMe-C₆H₃(OH)·CHO, MeOH, and 50% aq. KOH, (I) gives 2 : 4-dimethoxyphenyl 2'-hydroxy-6'-methoxy-, m.p. 116.5°, 2'-hydroxy-3'-methoxy-, m.p. 117°, and 2'-hydroxy-5'-methoxy-styryl ketone, m.p. 129°, respectively. 2 : 4 : 1-(OH)₂C₆H₃·COMe and (II) similarly give 2 : 4-dihydroxyphenyl 2'-hydroxy-3'-methoxystyryl ketone, m.p. 211°. Varying yields of the above substances under varying conditions are reported. E. W. W.

Functional aptitude of the methyl group. IV. Derivatives of acetophenone and chalkone. L. CHARDONNENS and J. VENETZ (Helv. Chim. Acta, 1939, 22, 1278—1286; cf. A., 1939, II, 419).—Interaction of 3 : 4 : 1-NO₂·C₆H₃·COMe (I) and *p*-NO₂·C₆H₄·NMe₂ (II) in boiling EtOH containing Na₂CO₃ gives a very complex mixture of products which appear to be formed by changes involving both Me groups; under these conditions C₆H₅Me does not react. *m*-NO₂·C₆H₄·COMe and (II) yield a very small amount of 3-nitrophenylglyoxal-ω : p'-dimethylaminoanil, m.p. 170° after softening; under like conditions *p*-NO₂·C₆H₄·COMe gives a rather better yield of the 4-NO₂-isomeride, m.p. 158—160°, whilst *o*-NO₂·C₆H₄·COMe gives only 4 : 4'-bisdimethylaminoazoxybenzene, m.p. 242°, which arises from (II). PhCHO and (I) in aq. EtOH containing NaOH at room temp. or at 140° in presence of a little piperidine give 2-nitro-*p*-tolyl styryl ketone, m.p. 151—152°, which condenses with (II) in COMe-EtOH containing Na₂CO₃ to 2-nitro-4-cinnamoylbenzal-4'-dimethylaminoanil, decomp. ~210° (yield 38%), and with PhCHO containing piperidine at 190—200° to 2-nitro-4-cinnamoylstyrylbenzene, m.p. 164—165°. 2 : 6-Dinitro-*p*-toluoyl chloride, m.p. 59—60°, from the acid and SOCl₂, is converted by condensation with CHAcNa·CO₂Et and hydrolysis of the product with H₂SO₄ into 3 : 5-dinitro-4-methylacetophenone, b.p. 198—200°/15 mm., m.p. 66—67° [*phenylhydrazone*, m.p. 255° (decomp.)]. This condenses with PhCHO in presence of piperidine at 140° to 2 : 6-dinitro-4-cinnamoyltoluene, m.p. 206—207° (yield 58%), transformed by PhCHO at 170° into 2 : 6-dinitro-4-cinnamoylstyrylbenzene, m.p. 191°. The yield is scarcely better than that obtained with the (NO₂)₂-derivative, possibly owing to the thermal instability of the chalkones. H. W.

Benzoylformic acid from styrene. C. D. HURD, R. W. MCNAMEE, and F. O. GREEN (J. Amer. Chem. Soc., 1939, 61, 2979—2980).—BzCO₂H is readily obtained from styrene (≠50% pure) by KMnO₄-NaOH at 70°. R. S. C.

Mixed magnesium alkoxides and their molecular compounds. IV. Action of ketones on ethereal magnesium butoxyiodide. V. M. TOLSTOPIATOV and A. T. RISKALTSCHUK (J. Gen. Chem. Russ., 1939, 9, 1148—1150).—MgI·OBu^α (I) in Et₂O and *p*-C₆H₄Me·COPh yield MgI₂·3*p*-C₆H₄Me·COPh.

In these conditions fluorenone and $\text{CO}(\text{CH}:\text{CHPh})_2$ give 1 : 1 compounds with (I). R. T.

4 : 4'-Dihydroxy-3 : 3'-dimethylbenzophenone. M. H. HUBACHER (J. Amer. Chem. Soc., 1939, 61, 2664—2665).—Contrary to Doebner *et al.* (A., 1890, 898), *o*-cresol-benzoin or -phthalein with KOH at 260—265° gives 4 : 4'-dihydroxy-3 : 3'-dimethylbenzophenone, m.p. 247—247.8° [diacetate, m.p. 106.8—107.2°; Me_2 , m.p. 203.7—204.2°, and Me_2 ether, m.p. 113.7—114.2° (oxime, m.p. 160.9—161.2°)], slowly converted by KOH at 280° into *o*-cresol and 4 : 3 : 1- $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$. M.p. are corr. R. S. C.

Preparation of nitrophenyl α -naphthyl ketones. J. S. JOFFE and S. S. BRAVINA (J. Gen. Chem. Russ., 1939, 9, 1133—1135).—*m*- or *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ and C_{10}H_8 yield (Friedel-Crafts) *m*-, m.p. 124° (lit. 117°) (phenylhydrazones, m.p. 194°), and *p*-nitrophenyl α - C_{10}H_7 ketone, m.p. 89° (lit. 95°). R. T.

Substituted ring compounds. I. Synthesis of 2 : 2 : 4-trimethylcyclopentanone. M. QUDRATI-KHODA and S. K. GHOSH (J. Indian Chem. Soc., 1939, 16, 287—295).— $\text{COMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ (I) (semicarbazone, m.p. 165°) with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ and Mg in C_6H_6 gives (dil. H_2SO_4) *Et* $\alpha\alpha\gamma$ -trimethylbutyrolactone- γ -acetate, b.p. 148—150°/7 mm. (with a product, b.p. 170—175°/6 mm.), which with PCl_5 followed by EtOH yields *Et*₂ γ -chloro- $\alpha\alpha\gamma$ -trimethyladipate, b.p. 113—115°/5 mm., reduced (Zn-AcOH) to the *Et*₂ ester (II), b.p. 145—146°/16 mm., of $\alpha\alpha\gamma$ -trimethyladipic acid (III), m.p. 80°. Alternatively, (I) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (piperidine; Na_2SO_4) give *Et*₂ α -cyano- $\beta\delta$ -dimethyl- Δ^4 -pentene- $\alpha\delta$ -dicarboxylate, b.p. 162°/4 mm., reduced (Al-Hg in $\text{Et}_2\text{O}\cdot\text{H}_2\text{O}$) to *Et*₂ α -cyano- $\beta\delta$ -dimethylpentane- $\alpha\delta$ -dicarboxylate, b.p. 155—156°/8 mm., which is hydrolysed (conc. HCl) to (III). With $\text{NaOEt}\cdot\text{EtOH}$, (II) gives *Et* 2 : 2 : 4-trimethylcyclopentanone-5-carboxylate, b.p. 88—90°/5 mm., converted by boiling dil. HCl into 2 : 2 : 4-trimethylcyclopentanone (IV), b.p. 65—66°/45 mm. (semicarbazone, m.p. 173°; 5- CHPh derivative, m.p. 125—126°). The compound obtained by Wallach (A., 1916, i, 487) from the dibromodihydroisophorone (V), m.p. 90°, and regarded by him as 2 : 4 : 4-trimethylcyclopentanone, is identical with (IV); intermediate products in its prep. from (V) (now regarded as 2 : 2-dibromo-3 : 3 : 5-trimethylcyclohexanone) are 3 : 3 : 5-trimethylcyclohexane-1 : 2-dione, m.p. 168—169° (Wallach, m.p. 89—90°), and 2 : 2 : 4-trimethylcyclopentan-1-ol-1-carboxylic acid, m.p. 90° (cf. *loc. cit.*). E. W. W.

Tetrahydrocitrilidene- and citronellylideneacetic acids. Syntheses of *sec*-isooctylcyclopentane derivatives. H. N. RYDON (J.C.S., 1939, 1544—1549).—Tetrahydrocitril, $\text{CH}_2(\text{CO}_2\text{H})_2$, and (a) $\text{N}[(\text{CH}_2)_2\cdot\text{OH}]_3$ or (b) $\text{C}_5\text{H}_9\text{N}$ give mixtures containing (a) 66% and (b) 25% of Δ^8 -isomeride, separated by preferential esterification of that isomeride, yielding 80-dimethyl- Δ^8 (I), b.p. 162°/13 mm. (*Et*, b.p. 134—135°/15 mm., and *p*-bromophenacyl ester, m.p. 39°), and Δ^4 -decenoic acid, b.p. 158—160°/7 mm. (*p*-bromophenacyl ester, m.p. 47°), equilibrated [47% of (I)] by $\text{NaOH}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. The structure of (I) is proved by oxidation to $\alpha\epsilon$ -dimethylheptic acid. In

conc. H_2SO_4 at room temp. (I) gives γ -*sec*-isooctyl- γ -butyrolactone, b.p. 158—162°/13 mm. When kept in $\text{HBr}\cdot\text{AcOH}$ at room temp. and then esterified, (I) gives (?) *Et* γ -bromo-80-dimethyldecoate, b.p. 145—150°/1.5 mm., obtained also from the lactone by $\text{HBr}\cdot\text{EtOH}$ and condensing poorly with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$. Partial esterification of citronellylideneacetic acid gives 80-dimethyl- Δ^8 -decadienoic acid, b.p. 173—175°/13 mm., and 28% of *Et* 80-dimethyl- Δ^8 -decadienoate, b.p. 139—141°/13 mm., hydrolysed to the Δ^8 -acid (II), b.p. 163—165°/1 mm. Equilibration by alkali gives 75% of (II). The K derivative of *Et* cyclopentanone-2-carboxylate and $\text{Pr}^B\cdot[\text{CH}_2]_3\cdot\text{CHMeI}$ (III) in boiling xylene give *Et* 2-*sec*-isooctylcyclopentanone-2-carboxylate, b.p. 165—175°/14 mm., converted by boiling aq. $\text{Ba}(\text{OH})_2$ into 2-*sec*-isooctylcyclopentanone (IV), b.p. 134—136°/16 mm. (2 : 4-dinitrophenylhydrazones, m.p. 86—87°), and α -*sec*-isooctyladipic acid, m.p. 54° [with $\text{Ba}(\text{OH})_2$ at 350—360° gives 52% of (IV)]. MgMeI in Et_2O converts (IV) into a carbinol, dehydrated by boiling aq. $\text{H}_2\text{C}_2\text{O}_4$ to yield 1-methyl-2-*sec*-isooctyl-(Δ^1)-cyclopentene, b.p. 112—115°/18 mm. Grignard condensation of (III) and cyclopentanone failed. *cyclo*Pentyl bromide, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and $\text{NaOEt}\cdot\text{EtOH}$ give *Et* cyclopentylacetoacetate, b.p. 125—130°/18 mm. (yields 4-cyclopentyl-1-phenyl-3-methyl-5-pyrazolone, m.p. 133—134°), which with $\text{NaOEt}\cdot\text{EtOH}\cdot\text{MeI}$ gives *Et* cyclopentylmethylacetoacetate, b.p. 128—131°/13 mm., hydrolysed by 10% aq. KOH to α -cyclopentylmethyl *Me* ketone, b.p. 76—79°/17 mm. (semicarbazone, m.p. 98°). R. S. C.

Catalytic oxidation of cycloheptylamine. V. S. SMIRNOV (J. Gen. Chem. Russ., 1939, 9, 1283—1285).—*cyclo*Heptylamine on oxidation with O_2 in presence of Cu-bronze affords suberone in yields up to 64%. G. A. R. K.

Products of the cyclising dehydration of 1- β -phenylethylcyclohexanol and synthesis of spirocyclohexane-1 : 1-indan-3-one. M. LEVITZ, D. PERLMAN, and M. T. BOGERT (Science, 1939, 90, 114—115).—Formulae showing the stages in the synthesis of spirocyclohexane-1 : 1-indan-3-one, m.p. 58—59° [oxime (I), m.p. 137—137.8°; NO_2 -derivative, m.p. 192°, also obtained by nitration ($\text{KNO}_3\cdot\text{H}_2\text{SO}_4$) of (I) and subsequent hydrolysis], are given. The product from 1- β -phenylethylcyclohexanol and 85% H_2SO_4 , when oxidised and oximated, affords (I) and oximes, m.p. 187—188° and 123—124° (derived NO_2 -ketone, m.p. 149—150°); the oxime, m.p. 177°, of Cook *et al.* (A., 1939, II, 103) could not be isolated. The oxime, m.p. 187.5° (Cook), may be that of *trans*-keto-octahydrophenanthrene. M.p. are corr.

L. S. T.

Sulphonation. IV. Sulphonation of benzanthrone. J. S. JOFFE and N. N. MELTEVA. **V. Sulphonation of phenyl α -naphthyl ketone.** J. S. JOFFE and G. Z. NAUMOVA (J. Gen. Chem. Russ., 1939, 9, 1104—1108, 1121—1123).—IV. Benzanthrone and 22% oleum (24 hr. at room temp.) yield a mixture of benzanthrone-2- and -3-sulphonic acid (quinine salts, m.p. 80—82° and 240—242°, respectively). A mixture of disulphonic acids is obtained by sulphonation with 100% H_2SO_4 at 170°.

V. α -C₁₀H₇-COPh and 95% H₂SO₄ at 160—170° afford BzOH and C₁₀H₆(SO₃H)₂. With 10% oleum at room temp. the product is 1 : 5-C₁₀H₆Bz·SO₃H.

R. T.

Spirans. XXIII. Derivatives of phenylindanedione. D. RĂDULESCU and F. BĂRBULESCU (Bul. Soc. Chim. România, 1938, 20, 29—37; cf. A., 1938, II, 31).—When bis-1 : 3-diketo-2-hydrindenyl (I) (1 mol.) and KOH-EtOH (2 mols.) are evaporated to dryness and the resulting K₂ salt is boiled with Br·[CH₂]₃·Br (II) (1 mol.) in PhOMe, 2 : 2'-trimethylenebis-1 : 3-diketo-2-hydrindenyl, m.p. 253°, is obtained. Replacement of (II) by *o*-C₆H₄(CH₂Br)₂ leads to 2 : 3-diphthaloyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 268° (becomes yellow in light), which in KOH-EtOH gives a transient blue colour and then a colourless substance, m.p. 285°. Although these products are colourless, substituted 2 : 2'-diaminobis-1 : 3-diketo-2-hydrindenyls and 2-amino-1 : 3-diketohydrindenyls are yellow and very feebly basic, which confirms the structure ascribed to the product obtained from (CH₂NH₂)₂ (A., 1924, i, 215). The 2 : 2'-Br₂-derivative of (I) with NHEt₂ in boiling abs. EtOH gives bis-2-dielhylamino-1 : 3-diketo-2-hydrindenyl, m.p. 219°, yellow. 2-Bromo-1 : 3-diketo-2-phenylhydrindene and an excess of the appropriate amine (even in a little boiling EtOH or C₆H₆ give 2-anilino- (III), m.p. 212°, 2-p-toluidino- (IV), m.p. 195°, and 2-1'-piperidino-1 : 3-diketo-2-phenylhydrindene, m.p. 142°, and 1 : 4-di-1' : 3'-diketo-2'-phenyl-2'-hydrindenylpiperazine, m.p. 275°, with varying amounts (even in absence of air) of bis-1 : 3-diketo-2-phenyl-2-hydrindenyl, m.p. 210°, which is obtained with a product, m.p. 277°, also by photochemical oxidation of 1 : 3-diketo-2-phenylhydrindene in EtOH. Hot KOH-EtOH hydrolyses (III) and (IV) to *o*-carboxyphenyl α -anilino-, m.p. 175° (decomp.) (Na and Ba salts), and α -toluidino-benzyl ketone (K salt), respectively, ring-closure of which could not be effected. R. S. C.

Sterols. LXXIV. Acetic acid derivatives of oestrone and α -oestradiol. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 2974).— $\Delta^{1:3:5}$ -Estratrien-17-on-3-oxoacetic, m.p. 209—211° [oxime, m.p. 230—232° (decomp.); Me ester, m.p. 130—132°], α - $\Delta^{1:3:5}$ -estratrien-17-on-3-oxopropionic, m.p. 195—198° (Me ester, m.p. 137—139°), and $\Delta^{1:3:5}$ -estratrien-17(α)-ol-3-oxoacetic acid, m.p. 182—184° (Me ester, m.p. 94—96°), are prepared by condensing the appropriate alcohol and CH₂Cl·CO₂Et by boiling NaOEt-EtOH (excess) and subsequently hydrolysing by KOH-EtOH. R. S. C.

Δ^5 -3-Hydroxy-7-keto α tiocolenic acid and related compounds. T. REICHSTEIN and H. G. FUCHS (Helv. Chim. Acta, 1939, 22, 1160—1170).—Me Δ^5 -3(β)-acetoxy α tiocolenate is oxidised by CrO₃ in AcOH at 55° to Me Δ^5 -7-keto-3(β)-acetoxy α tiocolenate (I), m.p. 182—186° (corr.), [α]_D²⁵ -74.8 \pm 2°, [α]_D²⁵ -89.7 \pm 3° in COMe₂, and some Me Δ^5 -7-keto α tiocoladienoate, m.p. 197—199° (corr.), also obtained from boiling MeOH-HCl and (I). Hydrogenation (PtO₂ in AcOH) of (I) gives a mixture of Me 7(α + β)-hydroxy-3(β)-acetoxy α tiocolenate, which is oxidised (CrO₃ in AcOH) at 30° to Me 7-keto-3(β)-acetoxy α tiocolenate, m.p. 176—179° (corr.), and

is converted by Ac₂O in C₅H₅N at 70—80° into Me 3(β) : 7(α)- (II), m.p. 147—149° (corr.), [α]_D²⁵ +64.1 \pm 6°, [α]_D²⁵ +77.7 \pm 6° in COMe₂, and 3(β) : 7(β)- (III), m.p. 159—162° (corr.), [α]_D²⁵ -3.1 \pm 1°, [α]_D²⁵ -2.30 \pm 1.5° in COMe₂, -diacetoxy α tiocolcholanate. (II) is hydrolysed by KOH-aq. MeOH to 3(β) : 7(α)-dihydroxy α tiocolcholanate, m.p. 252—257° (corr.; decomp.) [Me ester (IV), m.p. 194—197° (corr.)], transformed by Ac₂O and C₅H₅N at 100° into the 3(β) : 7(α)-Ac₂ acid, m.p. 237—241° (corr.), whereas (III) yields 3(β) : 7(β)-dihydroxy α tiocolcholanate, m.p. ~230° [Me ester (V), m.p. 224—229° (corr.)]. (IV) or (V) is oxidised by CrO₃ in AcOH at room temp. to Me 3 : 7-diketo α tiocolcholanate, m.p. 194—197° (corr.). This is reduced by Zn-Hg and conc. HCl to α tiocolcholanate, m.p. 228—230° (corr.) [Me ester, m.p. 143—144° (corr.)]. H. W.

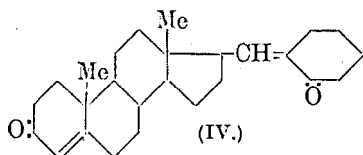
Constituents of the adrenal cortex and related substances. XXVIII. *allo*Pregnane-3 : 21-diol-20-one diacetate and *allopregnan*-21-ol-3 : 20-dione acetate. T. REICHSTEIN and J. VON EUW (Helv. Chim. Acta., 1939, 22, 1209—1212).—3-Acetoxy α tiocolcholanate is converted by the successive actions of SOCl₂ at 5° and CH₂N₂ in abs. Et₂O at -10° into 21-diazo*allopregnan*-3-ol-20-one acetate, m.p. 134—134.5° (decomp.), which with KOH-H₂O-MeOH at room temp. gives 21-diazo*allopregnan*-3-ol-20-one, m.p. 170—172° (decomp.), converted by AcOH at 95—100° into 21-acetoxy*allopregnan*-3-ol-20-one (I), m.p. 202—204°, which with Ac₂O-C₅H₅N at room temp. yields the 3 : 21-diacetate, m.p. 151—152.5° after becoming opaque at 90—100°. CrO₃ in AcOH oxidises (I) to *allopregnan*-21-ol-3 : 20-dione acetate, m.p. 197—199°. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XXIX. Action of lead tetra-acetate on *allopregnanolone* acetate, *pregnenolone* acetate, and *progesterone*. T. REICHSTEIN and C. MONTGEL (Helv. Chim. Acta, 1939, 22, 1212—1221; cf. Ehrhart *et al.*, A., 1939, II, 327).—*allopregnan*-3-ol-20-one acetate is oxidised by Pb(OAc)₄ in glacial AcOH preferably containing Ac₂O at 68—70° mainly to *allopregnan*-3 : 21-diol-20-one diacetate, m.p. 152—153.5°, with ~2% of (?) *allopregnan*-3(β) : 17(β) : 21-triol-20-one triacetate (I), m.p. 190—192° (corr.). Hydrolysis of (I) by KHCO₃ in aq. MeOH at room temp. followed by oxidation of the product with HIO₄ and subsequent energetic hydrolysis leads to 3(β) : 17(β)-dihydroxy α tiocolcholanate, m.p. 272—274° (corr.; decomp.) [Me ester, m.p. 238—242° (decomp.)]. Similarly *pregnenolone* acetate gives mainly *pregnen*-3 : 21-diol-20-one diacetate, m.p. 164—165° (corr.), and a (?) *pregnenetriolone* triacetate, m.p. 182—185° (corr.). Contrary to B.P. 502,474 (B., 1939, 995) and Ehrhart (*loc. cit.*) it has not been found possible to isolate deoxycorticosterone acetate as the main product of the oxidation of progesterone; refined methods of isolation result in a yield of ~3% but the method has no practical significance. H. W.

Steroids and sex hormones. LVII. Addition of aniline to Δ^5 -17-acetylenylandrosterone-3 : 17-diol. M. W. GOLDBERG and R. AESCHBACHER (Helv. Chim. Acta, 1939, 22, 1188—1190).— Δ^5 -17-

Acetylenylandrostene-3 : 17-diol, HgCl_2 , and NH_2Ph at $60-70^\circ$ give Δ^5 -3 : 17-dihydroxypregnenone-20-anil (I), m.p. $190-192^\circ$, $[\alpha]_D^{20} -197.5 \pm 2^\circ$ in CHCl_3 , oxidised by $\text{Al}(\text{O}i\text{Bu})_3$ in boiling C_6H_6 - COMe_2 to Δ^4 -3-keto-17-hydroxypregnenone-20-anil, m.p. $221-223^\circ$, $[\alpha]_D^{20} -19 \pm 1^\circ$ in CHCl_3 . Δ^5 -3 : 17-Diacetoxypregnenone-20-anil has m.p. $207-209^\circ$, $[\alpha]_D^{20} -155 \pm 2^\circ$ in CHCl_3 . All m.p. are corr. (vac.).

H. W.
Steroids. XXIII. Homologues of the testicular hormone. I. K. MIESCHER and A. WETTSTEIN (Helv. Chim. Acta, 1939, 22, 1262-1268; cf. A., 1939, II, 431).—Addition of EtOH to Me Δ^5 -3-hydroxy Δ^5 -etiocholenate (I) and finely divided Na in xylene at $160-170^\circ$ gives Δ^5 -17-hydroxymethyl-androsten-3-ol (II), m.p. $209-211^\circ$ (diacetate, m.p. $136-137^\circ$), and a little Δ^5 -3-hydroxy Δ^5 -etiocholenic acid. Successive bromination, oxidation (CrO_3 , AcOH), and debromination of (II) leads to Δ^4 -3-keto Δ^5 -etiocholenic acid (III), m.p. $258-262^\circ$ [Me ester, m.p. $134-135^\circ$, also obtained by treatment of (I) with $\text{Al}(\text{O}i\text{Pr})_3$ in boiling PhMe-cyclohexanone]. (II) is dehydrogenated by $\text{Al}(\text{O}i\text{Pr})_3$ and the ketone fraction is isolated by



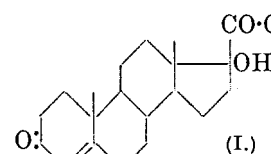
Girard's reagent; it is separated by $(\text{CH}_3\text{CO})_2\text{O}$ into the doubly unsaturated ketone (IV), m.p. $190-193^\circ$, which with $1:4\text{-C}_{10}\text{H}_6(\text{OH})_2$ gives a marked yellow colour with intense green fluorescence, and Δ^4 -17-hydroxymethyl-androsten-3-one (V), m.p. $158-159^\circ$ [acetate, m.p. $114-115^\circ$ (semicarbazone, m.p. $214-215^\circ$)], which does not give a colour with $1:4\text{-C}_{10}\text{H}_6(\text{OH})_2$. Oxidation (CrO_3 in AcOH) of (V) yields (III). M.p. are corr. H. W.

Steroids and sex hormones. LVI. Transformation of Δ^5 -17-acetylenylandrostene-3 : 17-diol into progesterone. M. W. GOLDBERG and R. AESCHBACHER (Helv. Chim. Acta, 1939, 22, 1185-1188).—Successive treatments of Δ^5 -17-acetylenylandrostene-3 : 17-diol with $\text{Hg}(\text{NHAc})_2$ in boiling abs. EtOH and H_2S give Δ^5 -16,3-hydroxypregnadien-20-one, m.p. $211-213^\circ$ [acetate, m.p. $175-177^\circ$, $[\alpha]_D^{20} -30.1 \pm 1.5^\circ$ in 95% EtOH; oxime, m.p. $219-220^\circ$ (decomp.)], hydrogenated to Δ^5 -3-hydroxypregnen-20-one, which is oxidised (Oppenauer) to progesterone, m.p. 127° , $[\alpha]_D^{20} +185.3 \pm 2.5^\circ$ in 95% EtOH.

H. W.
Sterols. LXXI. Urane derivatives. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 2719-2722).—Urane-3 : 11-dione (I), Br, and a little HBr in AcOH give a (? 4-)Br-derivative, m.p. $202-203^\circ$ (decomp.), converted by boiling $\text{C}_5\text{H}_5\text{N}$ into a pyridinium salt, m.p. $>300^\circ$, which, when heated at $5-10$ mm., gives a *uredione*, m.p. $168-170^\circ$. H_2 -PtO₂ at $25^\circ/3$ atm. reduces (I) in abs. EtOH to uran-3(β)-ol-11-one (II), m.p. $205-208^\circ$ [acetate, m.p. $170.5-172^\circ$; CrO_3 gives (I)], as sole product. $\text{Al}(\text{O}i\text{Pr})_3$ -Pr^oOH also gives mainly (II),

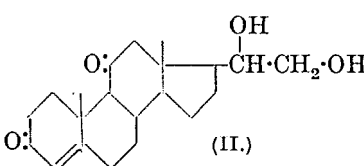
the *epi*-isomeride not being isolated. Urane-3 : 11-diol is oxidised by CrO_3 to (II), but by cyclohexanone- $\text{Al}(\text{O}i\text{Pr})_3$ in PhMe to uran-11-ol-3-one, m.p. $169.5-171^\circ$ [acetate, m.p. $195-197^\circ$; semicarbazone, m.p. $251-253^\circ$ (decomp.)]. Zn-HCl-EtOH reduces (I) to uran-11-one, m.p. $135-136.5^\circ$ (no semicarbazone), hydrogenated (PtO₂; AcOH; $25^\circ/3$ atm.) to uran-11-ol, m.p. $\sim 110^\circ$ (acetate, m.p. $140-142^\circ$). Zn-HCl-EtOH reduces uranetrione to urane-11 : 20-dione, m.p. $199-201^\circ$. R. S. C.

Constituents of the adrenal cortex and related substances. XXVI. Proof of the adherence of substance S to the 17(β)-series. T. REICHSTEIN, C. MEYSTRE, and J. VON EUW (Helv. Chim. Acta, 1939, 22, 1107-1113; cf. A., 1939, II, 77).—The annexed formula of substance S (I) is confirmed. (I) is converted by successive treatments with HIO_4



and $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$ into Me 17(β)-hydroxy-3-keto- Δ^4 -etiocholenate (II), m.p. $216-218^\circ$ (corr.). Saturation of the double linking of Me 3(β) : 17(α)-dihydroxy- Δ^5 -etiocholenate (III) with Br followed by cautious oxidation with CrO_3 and debromination with Zn affords Me 17(α)-hydroxy-3-keto- Δ^4 -etiocholenate, m.p. $182-185^\circ$ (corr.), which is very difficult to purify and is better obtained by oxidation of (III) with boiling COMe_2 - C_6H_6 and $\text{Al}(\text{O}i\text{Bu})_3$ followed by purification with Girard's reagent T. Although not obtained pure it is certainly not identical with (I). (II) is also obtained (Oppenauer) from Me 3(β) : 17(β)-dihydroxy- Δ^5 -etiocholenate. H. W.

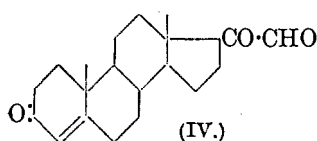
Constituents of the adrenal cortex and related substances. XXX. Substance T. T. REICHSTEIN and J. VON EUW (Helv. Chim. Acta, 1939, 22, 1222-1227; cf. A., 1938, II, 499).—The initial material consists of fractions C17, A2 and 3 (A., 1936, 1382) which are distributed (after hydrolysis with aq. MeOH-KHCO₃ at room temp.) between C_6H_6 and H_2O . Separation of the amorphous mixture present in C_6H_6 yields (after acetylation) the acetates of substances N, S, Fa, M, dehydrocorticosterone, corticosterone, and a diacetate (I), $\text{C}_{25}\text{H}_{34-36}\text{O}_6$, m.p. $212-213^\circ$ (corr.). (I) does not reduce alkaline Ag solution at room temp. and hence does not contain a ketol group. The absorption spectrum proves it to be an $\alpha\beta$ -unsaturated ketone. Hydrolysis of (I) with K_2CO_3 in aq. MeOH gives substance T



(II), which is oxidised by CrO_3 in AcOH to Δ^4 -3 : 11-diketoetiocholenic acid [Me ester, m.p. $178-180^\circ$ (corr.)]. Under similar conditions (I) is stable towards CrO_3 . H. W.

Constituents of the adrenal cortex and related substances. XXVII. Δ^4 -3-Ketoandrostenyl-17-glyoxal and related substances. H. REICH and T. REICHSTEIN (Helv. Chim. Acta, 1939, 22, 1124-1138).— Δ^5 -21-Chloro-3-hydroxypregnen-20-one (I) (improved prep.) is converted by $\text{C}_5\text{H}_5\text{N}$ at 100° into

the *pyridinium chloride*, m.p. 289—293° (corr.; decomp.) [corresponding bromide, m.p. ~300° (corr.; decomp.)], either of which is converted by $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot\text{NMe}_2$ in presence of alkali into $\Delta^5\text{-3-hydroxy}\Delta^4\text{-cholesterol-N-p-dimethylaminophenyl-nitrone}$ (+ H_2O), m.p. 133—134°. This is transformed by dil. HCl into $\Delta^5\text{-3-hydroxypregnen-20-one-21-al}$, two forms, (+ H_2O) m.p. 135—136° (corr.) and 170° (corr.), which are difficult to purify and are possibly different hydrates or polymerides. Both forms reduce Ag-diammine solution and gave the same Me_2 acetal (II), m.p. 112—113° (corr.), $[\alpha]_D^{25} + 39.1 \pm 1^\circ$, $[\alpha]_{534}^{25} + 52.2 \pm 1^\circ$ in MeOH, when treated with MeOH-HCl at room temp. or, more rapidly, when heated. A *dioxime*, m.p. 285—290° after becoming transformed into needles at ~225°, a *quinoxaline* derivative, $\text{C}_{27}\text{H}_{31}\text{ON}_2$, m.p. 229—231° after becoming converted into needles at 200°, and a *dianil*, m.p. 85—90°, have been prepared. (II) is oxidised by $\text{COMe}_2\text{-C}_6\text{H}_6$ and $\text{Al}(\text{OBu}^n)_3$ to $\Delta^4\text{-pregnene-3:20-dione-21-al Me}_2$ acetal, m.p. 84—86°, $[\alpha]_D^{25} + 170.3 \pm 2^\circ$, $[\alpha]_{534}^{25} + 207.9 \pm 3^\circ$ in COMe_2 , which has the absorption spectrum characteristic of $\alpha\beta$ -unsaturated ketones. Cautious hydrolysis with acids gives with difficulty impure (IV) (below). (I) is readily oxidised by COMe_2 and $\text{Al}(\text{OBu}^n)_3$ to 21-chloroprogesterone



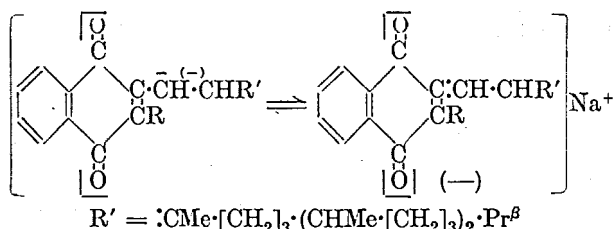
(III), m.p. 203—205° (corr.), $[\alpha]_D^{25} + 209.5 \pm 6^\circ$, $[\alpha]_{534}^{25} + 255.2 \pm 7^\circ$ in CHCl_3 , with, possibly, $\Delta^4\text{-3-keto}\Delta^4\text{-cholesteric acid [Me ester, m.p. 170—174° (corr.)]}$. (III) is converted by NaOAc-AcOH into deoxycorticosterone acetate, m.p. 159—160° (corr.), from which it is regenerated by PCl_5 and CaCO_3 in CHCl_3 . 21-Bromoprogesterone has m.p. 190—191° (decomp.). (III) yields the corresponding *pyridinium chloride*, m.p. 274—275° (corr.; decomp.), and bromide, m.p. 265—268° (corr.; decomp.), the former of which with $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot\text{NMe}_2$ gives $\Delta^4\text{-3-keto}\Delta^4\text{-cholesterol-N-p-dimethylaminophenyl-nitrone}$, m.p. 112—118°, converted by dil. HCl in Et_2O into $\Delta^4\text{-pregnene-3:20-dione-21-al}$ [$\Delta^4\text{-3-ketoandrosteryl-17-glyoxal}$] (IV), m.p. 104—106°. H. W.

Steroids. I. 6-Ketoprogesterone and the stereochemical configuration of several 3:5:6-triols. M. EHRENSTEIN (J. Org. Chem., 1939, 4, 506—518).—Androstan-5-ol-3:6:17-trione, m.p. 249.5—251° (decomp.), is obtained by direct oxidation of dehydroisoandrosterone (I) with CrO_3 in glacial AcOH, by transforming dehydroisoandrosterone acetate by H_2O_2 in AcOH into androstane-3(β):5:6-(trans)-triol-17-one, m.p. 295—298° (decomp.), which is oxidised further by CrO_3 , and by converting (I) by OsO_4 in Et_2O into androstane-3(β):5:6-(cis)-triol-17-one, m.p. 243—245.5°, $[\alpha]_D^{25} + 79.5^\circ$ in MeOH, which is oxidised by CrO_3 in AcOH. Pregnan-5-ol-3:6:20-trione (II), m.p. 267—268° (slight decomp.), is obtained by direct oxidation of $\Delta^5\text{-pregnen-3-ol-20-one}$ (III) with CrO_3 in AcOH. Alternatively (III) is transformed into its acetate, which is oxidised (30% H_2O_2 in AcOH) and then hydrolysed to pregnane-3(β):5:6-(trans)-triol-20-one, m.p. 256—258°, which is further oxidised by CrO_3 . In a third method (III) is oxidised

by OsO_4 in abs. EtOH or dioxan to pregnane-3(β):5:6-(cis)-triol-20-one, m.p. 231—232.5° after softening at 229°, $[\alpha]_D^{25} + 59.8^\circ$ in MeOH, which is further oxidised to (II). (II) is converted by HCl in CHCl_3 at 4° into $\Delta^4\text{-pregnene-3:6:20-trione}$ (6-ketoprogesterone), m.p. 185—188°. The stereochemical configurations of the substances are discussed. H. W.

5-Anilino-4-hydroxy-1:2-benzoquinone, m.p. 210° (decomp.), and prep. of 1:2:4- $\text{C}_6\text{H}_3(\text{OH})_3$.—See A., 1939, III, 1008.

The blue alkali salts of α -phyloquinone (vitamin- K_1) and similar compounds. P. KARRER (Helv. Chim. Acta, 1939, 22, 1146—1149).—Reasons are advanced for assigning the mesomeric formulæ:



to the blue salts of α -phyloquinone; related salts are discussed. H. W.

Derivative of vitamin- K_1 . H. J. ALMQUIST and A. A. KLOSE (J. Biol. Chem., 1939, 130, 791—793).—Description is given of the prep. of a compound, (?) $\text{C}_{31}\text{H}_{50}\text{O}_4$, from the oily pigment obtained by the alkaline hydrolysis of $-K_1$. During the hydrolysis no appreciable fission occurs but there is an increase in mol. wt. accompanied by the addition of 2 O and several H. At least one added O is phenolic. The absence of fission strongly indicates that the side structure is united to the 1:4-naphthaquinone nucleus by a C-C linking and for this group phytyl appears the only logical choice. The purest synthetic specimens of 2-methyl-3-phytyl-1:4-naphthaquinone have nearly the same activity as $-K_1$, with which they are probably identical. H. W.

Synthesis of iodinated benzoylbenzoic acids and anthraquinones. R. W. HIGGINS and C. M. SUTER (J. Amer. Chem. Soc., 1939, 61, 2662—2664).—4:5:1:2- $\text{C}_6\text{H}_2\text{I}_2(\text{CO})_2\text{O}$ (I) (1 mol.) and AlCl_3 (2.2 mols.) in boiling C_6H_6 give 80% of 4:5-di-iodo-2-benzoylbenzoic acid, m.p. 244—245°, converted by 100% H_2SO_4 at 140° (more dil. acid causes loss of I) into 2:3-di-iodoanthraquinone (80% yield), m.p. 291—292° (cf. Eckert et al., A., 1929, 701). Similarly are obtained (?) 3:4-, m.p. 223—224°, and 3:6-di-iodo-2-benzoylbenzoic acid, m.p. 218—220°, and thence 1:2-, m.p. 236—237°, and 1:4-di-iodoanthraquinone, m.p. 218—219°. 3:4:6:1:2- $\text{C}_6\text{H}_2\text{I}_3(\text{CO})_2\text{O}$ yields approx. equal amounts of 3:4:6- and 3:5:6-tri-iodo-2-benzoylbenzoic acid (acids, m.p. 257—258° and 225—227°, were isolated), each cyclised at 105° in 25% yield to 1:2:4-tri-iodoanthraquinone, m.p. 202—204°. $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ could not be caused to react with $m\text{-C}_6\text{H}_4\text{I}_2$. 3:4:5:6:1:2- $\text{C}_6\text{H}_2\text{I}_6(\text{CO})_2\text{O}$ or (I) reacts (AlCl_3) with PhOMe, o - or $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{OMe}$, but not with $o\text{-C}_6\text{H}_4(\text{OMe})_2$ or 4:1:2- $\text{C}_6\text{H}_3\text{Cl}(\text{OMe})_2$. I

in iodoanthraquinones is determined by Na-EtOH, followed by digestion of the crude AgI with dil. HNO₃. M.p. are corr. R. S. C.

o-Quinonemono-oxime inner complexes. H. M. HAENDLER [with G. MCP. SMITH] (J. Amer. Chem. Soc., 1939, 61, 2624—2626).—Adding the metal acetate in EtOH or H₂O to phenanthra-9 : 10-quinone-9-oxime in hot EtOH and adjusting the *p*_H by aq. NH₃ or AcOH to effect coagulation gives coloured complexes, $(C_{14}H_8\langle\begin{smallmatrix} O \\ \diagup \diagdown \\ N \cdot O \end{smallmatrix}\rangle)_2M$, in which M = Cd (unstable compound + xC₅H₅N), Cu, Pb, Mn, UO₂, anhyd. and + 2EtOH. Chrysenequinonemono-oxime gives similar complexes, in which M = Cu, Pb, Mn, Ni (prep. by NiCl₂), UO₂, anhyd. and + 2EtOH. Cr, Hg, Pd, Rh, and Zn also give complexes. Retenequinone- and 2- and 4-nitrophenanthraquinone-oximes also give complexes. R. S. C.

Sulphonation. VI. Sulphonation of 1 : 2-benzanthraquinone. J. S. JOFFE and E. N. KASCHNITZKAJA (J. Gen. Chem. Russ., 1939, 9, 1124—1127).—1 : 2-Benzanthraquinone and 95% H₂SO₄ at 140—150° yield a mixture of 1 : 2-benzanthraquinone-2'-, -3'-, and -4'-sulphonic acids. R. T.

Preparation of dibenzpyrenequinone. I. Reaction of benzanthrone with benzoyl chloride. N. K. MOSCHTSCHINSKAJA (J. Gen. Chem. Russ., 1939, 9, 1376—1379).—Benzanthrone, BzCl, and AlCl₃ at 125°/2 hr. yield a mixture of 2- and 3-benzoylbenzanthrone. The latter is converted quantitatively into dibenzpyrenequinone by passing O₂ through its melt with AlCl₃ and NaCl at 155—160°. R. T.

Effect of high-tension electrical discharge on catalytic reaction. IV, V. I. SETO and M. OZAKI (J. Soc. Chem. Ind. Japan, 1939, 42, 271—274B).—IV. *dl*- + *l*-Menthone (94%) + menthol (6%, free and combined), in paraffin oil, are reduced by H₂-Ni at 135—155° under ordinary pressures (apparatus : A., 1937, I, 470). The system is subjected to a high electric tension which promotes catalytic action of Ni and thus increases speed of reaction. Optimum conditions, viz., 145° for 3 hr., give 78.5% of menthol (I) (*dl*- + *dl*-neo + *iso*- + *neoiso*-menthol).

V. Thymol (II) at 140—160° for 2—3 hr. similarly gives 66—68% of (I). Initial formation of menthone (*dl*- + *iso*-menthone) suggests that (II) gives menthenol, converted into menthone and thence into (I). A. T. P.

***d*-Menthyl phenylurethane**, m.p. 112—113° (corr.), [α]_D²⁰ + 75.7° in CHCl₃, and 3 : 5-dinitrobenzoate, m.p. 153—154° (corr.), [α]_D²⁰ + 771° in CHCl₃, and glycuronide, m.p. 120—122°, [α]_D²⁰ + 6.4° in EtOH [NH₄ salt, m.p. 200—202° (decomp.), [α]_D²⁰ + 8.1° in H₂O].—See A., 1939, III, 998.

Intramolecular rearrangements occurring during the dehydration of ditertiary dicyclic glycols of the camphene series. I. L. J. BRIUSOVA (J. Gen. Chem. Russ., 1939, 9, 905—911).—2 : 3-Dihydroxy-2 : 3 : 4-trimethylcamphane, m.p. 132—135°, formed from 4-methylcamphoquinone and MeMgI, yields on dehydration (KHSO₄-Na₂SO₄; 5 hr. at

150—155°) a ketone, b.p. 126—127°/20 mm., characterised by a semicarbazone, C₁₄H₂₅ON₃, m.p. 193—194°. 2 : 3-Dihydroxy-2 : 3-dimethylcamphane similarly gives an unsaturated ketone, C₁₂H₂₀O, b.p. 104.8—105°/10 mm. (oxime, m.p. 108—112°), isolated through the semicarbazone, m.p. 180—181°. Reduction of the ketone with Na-EtOH gives the unsaturated alcohol, C₁₂H₂₂O, b.p. 122—123°/10 mm., and with H₂-Raney Ni, the saturated ketone, b.p. 110—110.5°/12 mm. Possible structures are discussed and it is concluded that dehydration of the glycols is accompanied by rupture of the dicyclic system and formation of monocyclic ketones. V. A. P.

Action of acetic acid on camphene in presence of boroacetic anhydride or acetic anhydride and boric trioxide. M. IMOTO (J. Soc. Chem. Ind. Japan, 1939, 42, 267—268B; cf. A., 1939, II, 434).—Camphene (I), AcOH, and B(OAc)₃ or Ac₂O-B₂O₃ at 110—120° for 23 hr. give esters, hydrolysed to *iso*-borneol (reaction A). The reaction is reversible; with *isobornyl* acetate (II) and Ac₂O-B₂O₃-AcOH at 110—120° for 22 hr. the amount of (II) is reduced from 97 to 67%, and some (I) is formed. Addition of H₂SO₄ to reaction A at 50—60° for 3—4 hr. gives increased yields. A. T. P.

Intramolecular asymmetric induction. A. MCKENZIE and A. D. WOOD (J.C.S., 1939, 1536—1544).—(–)-*Menthyl* H, m.p. 166—167°, [α]_D²⁰ –55.8° in EtOH, *di*-(–)-*menthyl*, m.p. 61—62°, [α]_D²⁰ –74° in EtOH, (–)-*bornyl* H (I), m.p. 178—179°, [α]_D²⁰ –28.9° in CHCl₃, and *di*-(–)-*bornyl* 4 : 4'-*dinitrodiphenate*, m.p. 201—202°, [α]_D²⁰ –46.9° in EtOH, are laevorotatory in all solvents and show no sign of intramol. asymmetric induction during prep. Similarly (I) gives (by way of the acid chloride, m.p. 48—49°) (+)-*bornyl* (–)-*bornyl* 4 : 4'-*dinitrodiphenate*, m.p. 212—213°, which is inactive although unesterified H ester has a slightly altered α. Kuhn's views (A., 1932, 269) are disputed on the basis of these and other facts. The following are also described. (–)-*Menthyl*, [α]_D²⁰ –81.3° in EtOH, and (–)-*bornyl* *m*-nitrobenzoate, m.p. 76—77°, [α]_D²⁰ –36.4° in EtOH; (–)-*dimenthyl* phthalate, [α]_D²⁰ –96.9° in EtOH; *di*-(–)-*bornyl* phthalate, new m.p. 104—105°, [α]_D²⁰ –82.9° in EtOH; *di*-*dl*-*bornyl* 4 : 4'-*dinitrodiphenate*, m.p. 200—201°, α 0. Cinchonine, m.p. 220—221°, [α]_D¹⁸ –185.6° in CHCl₃, quinidine, [α]_D^{20.5} –87° in CHCl₃, and quinine H 4 : 4'-*dinitrodiphenate*, m.p. 229—231°, [α]_D²¹ (anhyd.) +102.4°, (+2C₆H₆) +87.2° in CHCl₃. [α] of the esters for other solvents are also detailed. R. S. C.

New method of resolving a racemic compound. G. M. HENDERSON and H. G. RULE (J.C.S., 1939, 1568—1573; cf. A., 1938, II, 286).—By repeating the process previously described on activated lactose a complete micro-resolution of *dl*-*p*-phenylenebis-aminocamphor has been obtained. A partial resolution has been achieved in the case of β-naphtholazomandelic acid. F. R. S.

Vitexin. E. PÉTERI (J.C.S., 1939, 1635—1637).—Oxidation of vitexin (I) with H₂O₂, Fehling's solution, and K₃Fe(CN)₆ gives no new degradation products. Nitration (15% HNO₃) of (I) gives tetranitroapigenin.

Sublimation of (I) with Zn (vac.) gives a *polyphenol*, $C_{15}H_{12}O_6$, acetylated to triacetylapiogenin.

F. R. S.

Bitter principle from *Andrographis paniculata*, Nees. I. A. MOKTADER and S. S. GUHA-SIRCAR (J. Indian Chem. Soc., 1939, **16**, 333—338).—Andrographolide, $C_{20}H_{30}O_5$ (I), new m.p. 220° (decomp.), heated with aq. EtOH-KOH and acidified gives *isoandrographolic acid*, $C_{20}H_{32}O_6$, m.p. 156° [*Ba* salt, also obtained from (I) and aq. $Ba(OH)_2$], which with warm aq. NH_3 followed by HCl gives *andrographolic acid*, m.p. 180°. With Br, (I) in conc. HCl gives a *product*, $C_{20}H_{30}O_5Br_2$ (?), m.p. 128—140°, or in AcOH a *compound*, $C_{20}H_{30}O_5Br_2$ (?), m.p. 110—112°. In aq. HBr, (I) gives a *hydrobromide*, m.p. 117—124°; with HCl in AcOH a hydrochloride, m.p. 56—57°. $I-ICl_3$ shows only one double linking. With Pd-H₂ in MeOH (I) gives *dihydroandrographolide*, m.p. 205° (decomp.), and with $SnCl_2$ -HCl an *isomeride*, m.p. 200° (decomp.) (mixed m.p. 183—185°). When heated with Ac_2O -NaOAc for 5—10 min., (I) is unchanged, Gorter's Δ_3 derivative (A., 1914, i, 1204) not being obtained; after 1 hr., a *product*, $C_{40}H_{58}O_9$ (?), is formed. With $POCl_3$, (I) gives a *product*, m.p. 85—90° (decomp.), containing P and Cl, but lacking the CH_2O_2 group of (I); with $PhNCO$, (I) forms a *product*, m.p. 90—95°.

E. W. W.

Ethereal extract of bark of Cajaput tree. M. ISII and Y. OSIMA (J. Agric. Chem. Soc. Japan, 1939, **15**, 841—842).—Extraction of the bark of *Melaleuca leucadendron*, Linn., yields 20% of material which contains a resinol, *melaleucin*, $C_{28}H_{45}O_3$, m.p. 304° (*monoacetate*, m.p. 280°).

J. N. A.

Kikyo root. VIII. Constitutional formula of platycodigenin. IX. Mol. wt. of platycodigenin. M. TSUJIMOTO and R. SENJU (J. Agric. Chem. Soc. Japan, 1939, **15**, 857—861, 862—864; cf. A., 1939, II, 470).—VIII. Platycodigenin, m.p. 242—243°, $[\alpha]_D^{25} + 59.45^\circ$, is an unsaturated monobasic acid and gives a positive Liebermann sterol reaction. It can be purified by crystallisation of the K salt or by adsorption on Al_2O_3 and elution with $COMe_2$.

IX. Determination of mol. wt. by titration, Barger's method, micro-Pregl titration, and analysis of K salt confirms the formula $C_{30}H_{48}O_7$.

J. N. A.

Velocity of reaction of aldehydes with ammonia. I. Reaction of furfuraldehyde with ammonia. E. K. NIKITIN and M. A. ABRAMOVA (J. Gen. Chem. Russ., 1939, **9**, 1347—1355).—The velocity of formation of furfuramide at 12.5° is greatest when 2 vols. of a solution containing 27—30 g. of Na_2CO_3 and 7.5—8.5 g. of NH_3 per 100 ml. are added per vol. of aq. furfuraldehyde (I). The concn. of (I) solutions is determined by comparing the time required for appearance of turbidity with that found for solutions of known concn.

R. T.

Dihydro-1:4-pyrans. VI. Opening and closing of the ring. R. C. FUSON, R. E. CHRIST, and C. K. BRADSHAW (J. Org. Chem., 1939, **4**, 401—409).—Et α -hydroxy- δ -2:4:6-trimethylbenzoylsorbate (I) (*benzoate*, m.p. 109°) is hydrogenated (Raney Ni in

EtOH) and then hydrolysed by boiling 10% aq. Na_2CO_3 to 2-mesityl-5:6-dihydro-1:4-pyran-6-carboxylic acid (II), m.p. 149—150°, which is not hydrogenated in presence of PtO_2 , Ni, or Pt, is not reduced by Na-Hg, but is converted by boiling HI containing red P into adipic acid. (II) is unchanged by alkaline H_2O_2 but is oxidised by O_3 or boiling dil. HNO_3 to 2:4:6- $C_6H_2Me_3CO_2H$. Br in CCl_4 converts (II) into a *compound*, $C_{15}H_{17}O_3Br$, m.p. 139°. Treatment of (II) with conc. HNO_3 and conc. H_2SO_4 gives 3-nitro-2:3':5'-dinitromesityl-5:6-dihydro-1:4-pyran-6-carboxylic acid, m.p. 255° [*Me* ester (III), m.p. 162—163°]. Boiling MeOH containing conc. H_2SO_4 transforms (V) into *Me* α -hydroxy- δ -2:4:6-trimethylbenzoylvalerate, m.p. 43—44°. The crude ester obtained from (I) gives on alkaline hydrolysis an oily acid which is shown to contain α -hydroxy- δ -2:4:6-trimethylbenzoylvaleric acid by the isolation of the 1-naphthylurethane, $C_{26}H_{27}O_5N$, m.p. 145—146°. Under reduced pressure the acid can be distilled almost without residue but is converted under these conditions into (II). Oxidation by $KMnO_4$ of the hydrolysed pure ester and treatment of the non-cryst. acid with conc. H_2SO_4 -conc. HNO_3 affords 3:5:2:4:6-(NO_2)₂ $C_6Me_3CO_2H$. Nitration of the ester yields (III). With $MgPhBr$ the ester gives a *solid*, $C_{27}H_{30}O_3$, m.p. 134—135°, and a liquid which has not been identified. Liquid NH_3 converts the ester into the *amide*, m.p. 111.5—112.5°. Hydrogenation (PtO_2 in acidic EtOH) of (I) gives 10—15% of (II) and an oil from which by treatment with Na_2CO_3 , followed by p - $C_6H_4PhCH_2COBr$, *p*-phenylphenacyl δ -2:4:6-trimethylbenzoylvalerate, m.p. 79°, is isolated; fractional distillation of the oil and hydrolysis of the fraction of highest b.p. yields (?) α -keto- ϵ -hydroxy- ϵ -2:4:6-trimethylphenylhezoic acid, m.p. 81° (*phenylhydrazone*, m.p. 103—104°). δ -2:4:6-Trimethylbenzoylvaleric acid (IV), m.p. 60°, is obtained with α -di-2:4:6-trimethylbenzoylbutane, m.p. 106°, by the action of $AlCl_3$ on adipic anhydride and mesitylene in CS_2 . Bromination of (IV) in CCl_4 at 0° affords the *compound*, $C_{15}H_{19}O_3Br$, m.p. 90—92°, whilst oxidation of it gives $(CH_2CO_2H)_2$ and mesitylgyloxylic acid.

H. W.

Structure of fluorescein, sulphonefluorescein, and their halogenated derivatives. R. B. SANDIN, A. GILLIES, and S. C. LYNN (J. Amer. Chem. Soc., 1939, **61**, 2919—2922).—Bromination (Phillips, A., 1932, 400) of fluorescein and sulphonefluorescein gives first the 4:5- Br_2 -derivatives, since hydrolysis of the products gives 2:1:3- $C_6H_3Br(OH)_2$. 4:5-Dibromofluorescein, m.p. 285°, gives a diacetate, m.p. 228—229° (lit. 211°). $SnCl_2$ -HCl in dioxan-AcOH (10:1) converts tetrabromofluorescein into 2:7-dibromofluorescein, m.p. 300—301° (*diacetate*, m.p. 259° after darkening), hydrolysed to 4:1:3- $C_6H_3Br(OH)_2$ and (?) o-5'-bromo-2':4'-dihydroxybenzoylbenzoic acid, m.p. 240—241° after darkening and sintering. 2:7-Dichloro-4:5-dibromofluorescein [prep. from the 2:7- Cl_2 -compound (I) (modified prep.) by Br (2 mols.)] similarly gives (I). These replacements indicate a fixed bond structure for the fluorescein derivatives.

R. S. C.

Simple hydroxychromans and hydroxycoumarans. P. KARRER, R. ESCHER, and H. RENTSCHLER (Helv. Chim. Acta, 1939, **22**, 1287—1291;

cf. A., 1938, II, 450; 1939, II, 174).— γ -Methyl- Δ^8 -butenyl bromide, from $\text{CH}_2\text{:CH}\cdot\text{CMc}_2\text{OH}$ and PBr_3 in light petroleum at -15° and subsequently at 10 – 15° , and trimethylquinol (I) in presence of ZnCl_2 give exclusively 6-hydroxy-2 : 5 : 7 : 8-pentamethylchroman, m.p. 95° . The prolonged action of $\text{COEt}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ on (I) in C_6H_6 at room temp. yields 4-hydroxy-3 : 5 : 6-trimethyl-1-ethylcoumarone, m.p. 108° , reduced (Pd-C in MeOH) to the corresponding coumarin (II), m.p. 120° (allophanate, m.p. 214°). (II) is obtained as by-product of the condensation of (I) with crotyl bromide. H. W.

Steric relationships of α -tocopherol and further investigation of the lower homologues of α -tocopherol. P. KARRER, H. KOENIG, B. H. RINGLER, and H. SALOMON (Helv. Chim. Acta, 1939, 22, 1139–1145; cf. A., 1939, II, 335).—The 3 : 5-dinitrobenzoate, allophanate, and *p*-nitrophenylurethane of *dl*- α -tocopherol (I) from synthetic phytol (II) have been further purified so that their m.p. agree with those of the corresponding compounds prepared from natural (II). The compounds are therefore identical and hence *dl*- α -tocopherol (III) from natural (II) is a racemic compound or mixture of racemic compounds with respect to the asymmetric centres δ and θ . Conclusions with regard to the spatial relationships in the aliphatic side-chain of natural (I) are not warranted since it is not impossible that racemisation occurs during the isolation of (II) from chlorophyll or that only a definite form of (IV) is used in the enzymic synthesis of (III) in the plant. The bromocamphorsulphonate of (I) has now been separated into a series of fractions of differing m.p. so that (I) is almost certainly a mixture of diastereoisomerides; it cannot at present be decided whether the sample, m.p. 52° , is identical with the derivative of natural (I). Biologically there appears no measurable difference between natural (I) and the diastereoisomeric forms of synthetic (I). (I) (5 : 7 : 8-trimethyltolol) is biologically the most active of all the tocopherols. Elimination of Me from the aromatic nucleus somewhat diminishes the activity (apparently least with 5 : 7-dimethyltolol) and replacement of Me by Et is accompanied by slight weakening of the activity. Improvements in the methods of preparing *dl*-5 : 8- and -7 : 8-dimethyltolol are recorded. H. W.

Vitamin-E. XIV. Absorption spectra of tocopherols, chromans, coumarans, and related compounds. T. J. WEBB, L. I. SMITH, W. A. BASTEDO, jun., H. E. UNGNADE, W. W. PRITCHARD, H. H. HOEHN, S. WAWZONEK, J. W. OPIE, and F. L. AUSTIN (J. Org. Chem., 1939, 4, 389–396).—The absorption spectra of *o*-allyl-, 3 : 5 : 6-trimethyl-2-allyl-, and 2 : 6-dihexenyl-phenol, 2 : 2-dimethyl-3 : 4-dihydrocoumaran, 1-methyl-1 : 2-dihydro- and 1 : 3 : 5 : 6-tetramethyl-1 : 2-dihydro-benzofuran, 6-methoxy-2 : 2 : 3-trimethyl-3 : 4-dihydro- and 6-hydroxy-2 : 2 : 5 : 7 : 8-pentamethyl-3 : 4-dihydro-coumaran, 4-hydroxy-1 : 3 : 5 : 6-tetramethyl-1 : 2-dihydro-benzofuran, 4-hydroxy-1 : 3 : 5 : 6-tetramethylbenzofuran, 6-hydroxy-5 : 7 : 8-trimethyl-3 : 4-dihydro- and 6-hydroxy-3-carbethoxy-7 : 8-dimethyl-coumarin, 6-hydroxy-2 : 5 : 7 : 8-tetramethyl-2-hexadecyl-3 : 4-dihydro- and 6-hydroxy-2 : 5 : 7-trimethyl-2-hexa-

decyl-3 : 4-dihydro-coumaran are described and discussed. H. W.

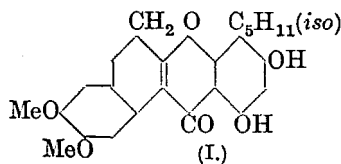
Vitamin-E. XV. Extension of the analytical method of Furter and Meyer. H. E. UNGNADE and L. I. SMITH (J. Org. Chem., 1939, 4, 397–400).—Examination of several simple chromans and coumarans by the colorimetric method of Furter and Meyer (A., 1939, III, 404) shows the method to be sp. for all tocopherols and for 6-hydroxychromans (I) generally. By this means it is possible to distinguish clearly between (I) and 4-hydroxycoumarans. H. W.

Constitution of natural tannins. VI. Colouring matters derived from 2 : 5-dihydroxyacetophenone. A. RUSSELL and S. F. CLARK (J. Amer. Chem. Soc., 1939, 61, 2651–2658; cf. A., 1937, II, 206).—Passage of dry HCl into an EtOAc solution of 2 : 5 : 1-(OBz) $_2$ C $_6$ H $_3$ ·COMe and 3 : 4 : 1-(OBz) $_2$ C $_6$ H $_3$ ·CHO at 0° for several days gives 2 : 5 : 3' : 4'-tetrabenzoyloxychalkone, m.p. 182 – 184° , hydrolysed by KOH (special procedure essential in this and other cases) to a mixture of 2 : 5 : 3' : 4'-tetrahydroxychalkone (I), m.p. 225 – 227° , and 6 : 3' : 4'-trihydroxyflavanone (II), m.p. 218 – 220° (decomp.). Solid (I) and (II) are stable, but in EtOH an equilibrium mixture is formed, containing, particularly when hot, much (II). Zn dust and HCl–EtOH reduce (II) alone or in admixture with (I) to bis-(6 : 3' : 4'-trihydroxy)flavopinacol, a light red amorphous material indistinguishable by colour reactions and in adsorption on hide powder from hemlock or mimosa tannins. Similar condensations using other aldehydes give 2 : 5 : 4'-tri-, m.p. 134 – 136° , 2 : 5 : 3'-tri-, m.p. 174 – 175° , 2 : 5 : 2'-tri-, m.p. 137 – 139° , 2 : 5 : 2' : 4'-tetra-, m.p. 137 – 139° , and 2 : 5 : 2' : 4' : 6'-penta-, an oil, -benzoyloxychalkone, 2 : 5 : 4'-tribenzoyloxy-3'-methoxychalkone, m.p. 145 – 147° , and 2 : 5 : 2' : 4'-tetrabenzoyloxy-6'-methylechalkone, m.p. 125 – 127° , and thence by hydrolysis 2 : 5 : 4'-, m.p. 222 – 224° , and 2 : 5 : 3'-trihydroxychalkone, m.p. 204 – 206° , 2 : 5 : 4'-trihydroxy-3'-methoxychalkone, m.p. 172 – 173° , 6 : 3'-, m.p. 234 – 236° , and 6 : 2'-dihydroxyflavanone, m.p. 178 – 180° (decomp.), 2' : 5'-di-, +0.5H $_2$ O, m.p. 175° (decomp.), 7 : 2' : 5'-tri-, +5.5H $_2$ O, m.p. 190° (decomp.), and 5 : 7 : 2' : 5'-tetra-hydroxy-2-phenylbenzopyrylium chloride, +2H $_2$ O, m.p. $>300^\circ$, and 7 : 2' : 5'-trihydroxy-2-phenyl-5-methylbenzopyrylium chloride, +H $_2$ O, m.p. 285 – 287° (decomp.). *m*-Benzoyloxybenzaldehyde, m.p. 37 – 38° , resorcydaldehyde dibenzoate, m.p. 98° , and orcydaldehyde dibenzoate, m.p. 134 – 135° , are also described. R. S. C.

Dunnione. I. J. R. PRICE and (Sir) R. ROBINSON (J.C.S., 1939, 1522–1529).—Partly a detailed account of work already reported (A., 1938, II, 375). Dunnione (I) [semicarbazone (II), m.p. 232 – 233° ; 2 : 4-dinitrophenylhydrazones, m.p. 266 – 268°] is probably 2 : 3 : 3-trimethyl-6 : 7-benzocoumaran-5 : 6-quinone, although other structures of the heterocyclic ring are possible, and its reactions are interpreted on this basis. With Zn dust and $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ it gives dihydrodunnione diacetate, m.p. 143 – 144° , which with $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ gives only (II). With *o*-C $_6$ H $_4$ (NH $_2$) $_2$ it gives a (?) phenazine, C $_{21}$ H $_{18}$ ON $_2$, dimorphic, m.p. 140 – 141° and $\sim 125^\circ$. It dissolves slowly in 5% aq. NaOH, from which the red chelated

Na salt is then removed by EtOAc or *iso*-C₅H₁₁-OH; immediate neutralisation gives a colourless solution, probably containing $\text{o-C}_6\text{H}_4\text{<CO-C-OH}$
 $\text{CO-C-CMe}_2\text{-CHMe-OH}$
 (becomes red at once with alkali), and an excess of acid regenerates (I). After (I) has been heated in alkali, acidification gives alloodunnione (II), $\text{o-C}_6\text{H}_4\text{<C-CO-O}$
 $\text{CO-C-CMe}_2\text{-CHMe}$, m.p. 161—162° [2:4-dinitrophenylhydrazone, m.p. 315° (decomp.) after darkening at ~290°], a mechanism for formation of which is suggested. When kept in 5% NaOH at room temp. or heated in 20% HCl, (I) gives α -dunnione [2:3:3-trimethyl-5:6-benzcoumaran-3:7-quinone], m.p. 120—122° (2:4-dinitrophenylhydrazone, m.p. 278—280°), converted by alkali into (I) and (II) and by conc. H₂SO₄ at 100° into β -isodunnione [4:4-dimethyl-7:8-benzchroman-5:6-quinone], m.p. 129—131°. With boiling 20% HCl this gives α -isodunnione [4:4-dimethyl-6:7-benzcoumaran-5:8-quinone], m.p. 118—119°. With KMnO₄, (I) gives $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$; with H₂O₂-aq. NaOH it gives MeCHO, $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, and (?) α -isopropylphthalide- α -carboxylic acid (III), m.p. 205—206°. With H₂O₂-aq. AcOH, (II) gives $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, but with aq. H₂O₂-NaOH it gives MeCHO and (III), formation of which is postulated as involving fission of two rings and loss of MeCHO by a reversed aldol change. Alkaline H₂O₂ generates $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and CMe₂ from lapachol or β -lapachone (2:4-dinitrophenylhydrazone, sinters at ~250°, m.p. 283—285°; with CrO₃ gives 0.59 AcOH). α -Lapachone-2:4-dinitrophenylhydrazone melts at 277—278°. CrO₃ forms 1.3 AcOH from (I) or (II) (proof of a Me in a side-chain and a CMe₂) and 0.5 AcOH from (III) (proof of CMe₂). R. S. C.

Sumatrol. II. Synthesis of dehydrotetrahydrosumatrol. T. S. KENNY, A. ROBERTSON, and (in part) S. W. GEORGE (J.C.S., 1939, 1601—1604).—Phlorisovalerophenone, m.p. 145° (improved prep.; 2:4-dinitrophenylhydrazone, m.p. 196°), is reduced (Zn-Hg) to isoamylphloroglucinol, m.p. 126°, which condenses with Me 2-cyanomethyl-4:5-dimethoxyphenoxyacetate, followed by hydrolysis, to give tetrahydrosumatrol, m.p. 206°, and a phenolic substance, C₂₂H₂₀O₅, m.p. 134° (acetate, m.p. 51°). The acid and Ac₂O-NaOAc yield *O*-diacetyl-, hydro-

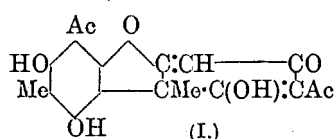


lysed to dehydrotetrahydrosumatrol (I), identical with the natural specimen. The probable structure suggested is (I). F. R. S.

Sterols. LXXIII. Reactions of digitogenin and gitogenin. R. E. MARKER and E. ROHRMANN (J. Amer. Chem. Soc., 1939, 61, 2724—2726).—Prep. of gitogenin (I), m.p. 266—268° [diacetate (II), m.p. 241—243°], from *Chlorogalum pomeridianum*, and of digitogenin (III) is described. (I) and (III) both form digitonides. Zn-Hg-HCl has no effect on (I) or (III). H₂-PtO₂ in AcOH at 70°/3 atm. gives dihydro-gitogenin, m.p. 195—197° (tri-*p*-nitrobenzoate, m.p. 189—191°; stable to SeO₂), and -digitogenin, m.p. 184—186°. SeO₂ oxidises (I) and (III). Br

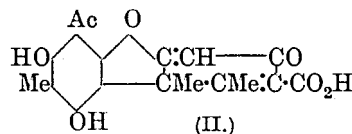
converts (II) into a Br-derivative, m.p. 219—220° (decomp.), reduced by Na in abs. EtOH to (I). CrO₃-AcOH at 95° oxidises (II) to gitogenin lactone diacetate, m.p. 248—251°, hydrolysed by KOH-EtOH to gitogenin lactone, m.p. 276—278° (dibenzoate, m.p. 275—278°). Similarly are obtained bromodigitogenin triacetate, m.p. 142° (decomp.), and digitogenin lactone, m.p. 279—282° (triacetate, m.p. 281—283°). R. S. C.

Usnic acid. VII. Analogues of usnic acid. R. T. FOSTER, A. ROBERTSON, and (in part) T. V. HEALY (J.C.S., 1939, 1594—1601).—A brief review



of the structures recently proposed for usnic acid (I) leads to the adoption of the expression shown, first suggested (Robertson,

et al., A., 1937, II, 347; cf. Asahina *et al.*, A., 1939, II, 32), and supported by the work of Schöpf and Ross (A., 1939, II, 82). A new structure for usnic acid (II) is deduced and its formation from (I) is discussed. The comparison of the analogues of (II)

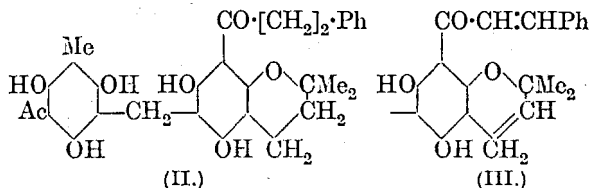


gives independent evidence in support of structure (II). 3-Methoxyphenoxyacetone (2:4-dinitrophenylhydrazone,

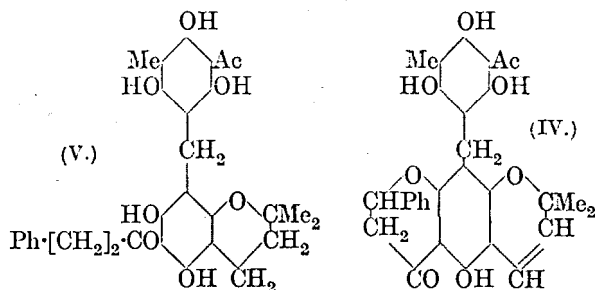
m.p. 146°) is cyclised to 6-methoxy-3-methylcoumarone, which with HCN-HCl gives the 2-formyl compound, m.p. 105° (2:4-dinitrophenylhydrazone, m.p. 262°). This aldehyde with hippuric acid-Ac₂O affords the azlactone, m.p. 194°, hydrolysed (NaOH) to 6-methoxy-3-methylcoumarone-2-pyruvic acid, m.p. 196° (oxime, m.p. 166°), which with H₂O₂ yields the -acetic acid, m.p. 145° (amide, m.p. 162°). The chloride of the acetic acid condenses with CH₂Ac-CO₂Et to give 6'-methoxy-3':3-dimethyl-2':3'-dihydrobenzofurano-(2':3':5:4)- Δ^2 -⁵-cyclohexadienone-2-carboxylic acid (+H₂O), m.p. 147° (Me ester, m.p. 101°; Et ester, m.p. 122°).

2-Hydroxy-4-methoxy-3-methylacetophenone and CH₂Br-CO₂Et-K₂CO₃ give Et 3-methoxy-6-acetyl-2-methylphenoxyacetate, b.p. 180—185°/15 mm. (2:4-dinitrophenylhydrazone, m.p. 167°; acid, m.p. 133°), which is cyclised to Et 6-methoxy-3:7-dimethylcoumarone-2-carboxylate, m.p. 75°, hydrolysed to the acid, m.p. 225° (decomp.). This acid with NaOAc-Ac₂O forms 6-methoxy-3:7-dimethylcoumarone, b.p. 92—93°/0.1 mm. (picrate, m.p. 92°), which with HCl-HCN yields the 2-formyl derivative, m.p. 102° (2:4-dinitrophenylhydrazone, m.p. 284°). The aldehyde condenses with hippuric acid to the azlactone, m.p. 218°, hydrolysed to 6-methoxy-3:7-dimethylcoumarone-2-pyruvic acid, m.p. 228° [oxime, m.p. 162° (decomp.)], and some 6-methoxy-2:3:7-trimethylcoumarone, m.p. 41° (reduced to the coumaran). Oxidation (H₂O₂) of the pyruvic acid gives 6-methoxy-3:7-dimethylcoumarone-2-acetic acid, m.p. 158° (amide, m.p. 179°), the chloride of which condenses with CH₂Ac-CO₂Et to form 6'-methoxy-3':7':3-trimethyl-2':3'-dihydrobenzofurano-(2':3':5:4)- Δ^2 -⁵-cyclohexadienone-2-carboxylic acid, m.p. 150° (Et ester, m.p. 115°). F. R. S.

Rottlerin. IV, V. Tetrahydroallorottlerin. A. MCGOOKIN, A. ROBERTSON, and E. TITTENSOR (J.C.S., 1939, 1579—1587, 1587—1593).—IV. Octahydrorottlerinone (I), previously assigned the structure of the H_2 -compound (cf. A., 1939, II, 485), is hydrolysed by 10% NaOH or NaOH-Zn to a mixture of 5 : 7-dihydroxy-8- β -phenylpropionyl-2 : 2-dimethylchroman, $Ph \cdot [CH_2]_2 \cdot CO_2H$, and 5 : 7-dihydroxy-2 : 2-dimethylchroman [bisbenzeneazo-derivative, m.p. 256° (decomp.)]. 5 : 7-Dihydroxy-8-acetyl-2 : 2-dimethylchroman and CH_2O give 5 : 7 : 5' : 7'-tetrahydroxy-8 : 8'-diacetyl-2 : 2 : 2' : 2'-tetramethyl-6 : 6'-dichromanylmethane, m.p. 240°, whilst the corresponding 8- β -phenylpropionyl compound similarly affords (I). *C*-Methylphloracetophenone with CH_2O gives 2 : 4 : 6 : 2' : 4' : 6'-hexahydroxy-5 : 5'-diacetyl-3 : 3'-dimethyldiphenylmethane, m.p. 291° (decomp.) [(OMe)₆-derivative, m.p. 103°], also obtained together with (I) from tetrahydrorottlerin (II) and AcOH. Re-investigation of a no. of derivatives of rottlerin (III) has not evaluated (III) as either $C_{30}H_{28}O_8$ or $C_{31}H_{30}O_8$ but mol. wt. determinations exclude formulæ based on C_{60} or C_{62} . The (OMe)₃-ether, m.p. 153°, of (II) and *O*-tetramethylrottlerinone, m.p. 136°, are described. The isolation of 2 : 4 : 6-trihydroxy-5-acetyl-3-methylazobenzene from (II) and diazoaminobenzene confirms the presence of *C*-methylphloracetophenone residue in (III). This residue is joined to the rest of the mol. by CH_2 and hence the structures (II) and (III) are assigned. The available evidence shows (III) not to contain a lactone group.



V. *iso*Rottlerin (IV) (cf. Brockmann *et al.*, A., 1938, II, 334) is hydrogenated, according to the conditions, to the H_2 -derivative and tetrahydroallorottlerin (V), m.p. 241°. Methylation (Me_2SO_4 - K_2CO_3) of (V) gives the (OMe)₅-derivative, m.p. 136°, which is hydrogenated (Pd-C) to *O*-pentamethyltetrahydroallorottlerin, m.p. 101°. Methylation of dihydroisrottlerin affords *O*-tetra-, m.p. 149°, and *penta*-methyl-dihydroisrottlerin, m.p. 135°. Diazoaminobenzene and (V) yield 2 : 4 : 6-trihydroxy-5-acetyl-3-methylazobenzene and 8-benzeneazo-5 : 7-dihydroxy-6- β -phenylpropionyl-2 : 2-dimethylchroman, m.p. 162°, identical



with a synthetic specimen, and not identical with either 6-benzeneazo-5 : 7-dihydroxy-8- β -phenylpropion-

yl-, m.p. 181°, or 8-acetyl-2 : 2'-dimethylchroman, m.p. 232°. These results indicate that (V) is constituted as shown. NaOH (4%) and (V) give octahydroallorottlerinone (VI), m.p. 175—175.5°, which has properties similar to those of (I). 5 : 7-Dihydroxy-6- β -phenylpropionyl-2 : 2'-dimethylchroman and CH_2O afford (VI), whilst the corresponding 6-Ac derivative gives 5 : 7 : 5' : 7'-tetrahydroxy-6 : 6'-diacetyl-2 : 2 : 2' : 2'-tetramethyl-8 : 8'-dichromanylmethane, m.p. 209°. The conversion of (III) into (V) by way of (IV) is explained and the structure which has been deduced for (IV) is supported by its behaviour on hydrogenation and methylation. F. R. S.

Cyclic acetals of furfuraldehyde. E. J. SALMI and I. J. JANSSON (Suomen Kem., 1939, 12, B, 28—30; cf. A., 1938, II, 427).—Equimol. amounts of furfuraldehyde (I) and $(CH_2OH)_2$ in hot C_6H_6 containing p - $C_6H_4Me \cdot SO_3H$ give the ethylene acetal (~70%), b.p. 91—93°/16 mm., of (I). Similarly prepared, the α -propylene (78%), α -butylene, and α -butylene acetal, have b.p. 97—99°/19—21 mm., 114.8—116.5°/16 mm., and 121.5—122.5°/18—20 mm., respectively. J. L. D.

Thio-compounds derived from *o*-aroylbenzoic acids. J. O'BROCKTA and A. LOWY (J. Amer. Chem. Soc., 1939, 61, 2765—2768).—Di- α -phenylphthalidyl sulphide (I), $(o-C_6H_4 \langle \begin{smallmatrix} CPh \\ CO \end{smallmatrix} \rangle)_2S$, m.p. 247°, is obtained from o - $C_6H_4Bz \cdot CO_2H$ (II) by P_2S_5 in hot C_6H_6 or alone at 115°, or from o - $C_6H_4Bz \cdot COCl$ and H_2S in hot C_6H_6 . It is converted by 5% KOH-EtOH, CrO_3 - or HNO_3 -AcOH, or $Pb(OAc)_2$ -EtOH- H_2O into (II). With H_2SO_4 , (I) gives anthraquinone. 30% H_2O_2 -AcOH converts (I) into (II) and α -phenylphthalide. Cu dust or Ag converts (I) in cymene into di- α -phenylphthalidyl, m.p. 265—266°. With $AlCl_3$ and C_6H_6 , (I) gives thiophenylphthalide, $o-C_6H_4 \langle \begin{smallmatrix} CPh \\ CO \end{smallmatrix} \rangle S$, m.p. 162°, converted by AcOH- H_2O_2 into α -diphenylphthalide and by P_2S_5 into dithiodiphenylphthalide. With P_2S_5 in boiling xylene, (II) gives 2-phenyl-3 : 4-benzthiophen, m.p. 236—237°. p - $C_6H_4Me \cdot CO \cdot C_6H_4 \cdot CO_2H$ -*o* and p - $C_6H_4Cl \cdot CO \cdot C_6H_4 \cdot CO_2H$ -*o* give similarly di- α -*p*-tolyl-, m.p. 212°, and di- α -*p*-chlorophenyl-phthalidyl sulphide, m.p. 232°, di- α -*p*-tolyl-, m.p. 247—248°, and di- α -*p*-chlorophenyl-phthalidyl, m.p. 247°, α -*p*-tolyl, m.p. 128°, and α -*p*-chlorophenyl-phthalide, m.p. 124°, and 2-*p*-tolyl-, m.p. 217°, and 2-*p*-chlorophenyl-3 : 4-benzthiophen, m.p. 241—242°. R. S. C.

Photo-oxidation of pyrrole. F. BERNHEIM and J. E. MORGAN (Nature, 1939, 144, 290).—Pyrrole dissolved in H_2O , EtOH, or $COMe_2$ and mixed with 0.5×10^{-4} M-methylene-blue (I) rapidly absorbs O_2 in light but not in the dark. The rate of O_2 uptake is a linear function of the light intensity, and effective λ lie between 5200 and 5800 Å. Eosin, but not fluorescein, can replace (I). No decarboxylation or decamination occurs. The cryst. product, C 49.1, H 5.3, N 14.1%, m.p. 102.5°, yield 58%, gives 72% of succinic acid and 14% of NH_3 -nitrogen on alkaline hydrolysis. *N*-Methyl- and -ethyl-pyrrole are also oxidised under the same conditions, but only 1 instead of 2 O per mol. is taken up. L. S. T.

Formation of 2:3:4:6-tetrabromopyridine during bromination of 2:6-dibromopyridine at about 500°. J. P. WIBAUT and A. F. BICKEL (Rec. trav. chim., 1939, 58, 994—997).—Bromination of 2:6-dibromopyridine in the gaseous phase, in presence of pumice, at 510—520°, gives 2:4:6-tribromo- and 2:3:4:6-tetrabromo-pyridine, m.p. 105.3—106° (cf. 2:3:5:6-isomeride, A., 1932, 1260), and a small amount of Br₅-derivative, m.p. 209—210°.

A. T. P.

Pyridine series. I. Improved synthesis of 2:3-dimethylpyridine and conversion of the latter into an analogue of thiamin. J. FINKELSTEIN and R. C. ELDERFIELD (J. Org. Chem., 1939, 4, 365—375).—Addition of Br·[CH₂]₃·OEt to CHAcNa·CO₂Et in abs. EtOH gives *Et* δ-methoxy-α-methylvalerate, b.p. 96—97°/13 mm., hydrolysed to the acid, b.p. 137—139°/11 mm. If the substances react in dioxan the product is *Et* α-methyl-α-γ-ethoxy-propylacetoacetate (I), b.p. 141—143°/16 mm., and an unidentified substance, b.p. 128—130°/0.5 mm. When heated with NaOH-aq. EtOH at 250° under H₂ at 1000 lb. per sq. in. (I) yields ζ-ethoxy-γ-methyl-n-hexan-β-one (II), b.p. 96—99°/17 mm., and a compound, b.p. 141—143°/17 mm. At 100° (II) is transformed by AcOH saturated with HBr at 0° into ζ-bromo-γ-methyl-n-hexan-β-one, b.p. 70—74°/1.5 mm., which is converted by 10% NH₃-abs. EtOH into the very hygroscopic 2:3-dimethyltetrahydro-pyridine (III), b.p. 154—157° (picrate, m.p. 154—157°). Dehydrogenation of (III) with Zn dust gives a small yield of 2:3-dimethylpyridine (IV), b.p. 162—164° (picrate, m.p. 187—188°). In model experiments it is shown that 2-methylpyridine (V) is converted into C₈H₅N by AgNO₃ in 10% AcOH at 180°, Me being lost, and that 2-methyl-5-ethylpiperidine is dehydrogenated by Pd-asbestos at 270—280° without loss of alkyl groups. In this manner (III) is satisfactorily dehydrogenated to (IV). Successive addition of PhBr, (V), and CH₂O to Li in abs. Et₂O leads to 2-β-hydroxyethylpyridine, b.p. 88—90°/2 mm. [platini-chloride, m.p. 176° (decomp.)], oxidised by boiling aq. KMnO₄ containing K₂CO₃ to picolinic acid. Similarly (IV) yields 3-methyl-2-β-hydroxyethylpyridine (VI), b.p. 94—95°/1 mm. (picrate, m.p. 137—138°). Addition of (VI) to a suspension of 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide in light petroleum at 100° gives 1-4'-amino-2'-methyl-5'-pyrimidylmethyl-2-β-hydroxyethylpyridinium bromide hydrobromide (VII), m.p. 240—245° (decomp.); 1-4'-amino-2'-methyl-5'-pyrimidylmethyl-3-methyl-2-β-hydroxyethylpyridinium bromide hydrobromide (VIII), m.p. 240—242° (decomp.), is obtained similarly. (VII) and (VIII) show no antipolyneuritic activity but approximate to the activity of thiamin as measured by carbon dioxide evolution in the yeast test.

H. W.

Derivatives of 2-aminomethyltetrahydroquinoline and -isoquinoline. A. GASSMANN and H. RUPE (Helv. Chim. Acta, 1939, 22, 1241—1262).—Gradual addition of BzCl to a solution of KCN and 6-methoxyquinoline, b.p. 146—148°/11 mm., m.p. 28°, in H₂O at 5° affords 6-methoxy-1-benzoyl-1:2-di-hydroquinoline-2-nitrile, m.p. 127°, converted by

NH₂OH in MeOH at -3° into the amidoxime, m.p. 148—149° (decomp.), and (?) 6-methoxyquinoline-2-nitrile, m.p. 176—177°, transformed by conc. HCl-Et₂O into the corresponding amide, m.p. 202—203° (hydrochloride, m.p. 237—238° after softening at 225°), and hydrolysed by boiling conc. HCl to 6-methoxyquinoline-2-carboxylic acid, m.p. 235—236° (decomp.) after softening at 233—234° (Na salt). (I) is reduced (freshly reduced Na in EtOAc) by H₂ at ~90°/120 atm. to 6-methoxy-2-benzamidomethyl-1:2:3:4-tetrahydroquinoline (II), m.p. 131—132° (NO-derivative, m.p. 138—139°). Boiling conc. HCl slowly hydrolyses (II) to 6-methoxy-2-aminomethyl-1:2:3:4-tetrahydroquinoline, b.p. 196—197°/12 mm. (tartrate, decomp. 195°; perchlorate, m.p. 278°; dihydrochloride, m.p. 224—225°), which is condensed with piperonal and then reduced (H₂ at 65°/100 atm.; Ni) to 6-methoxy-2-3':4'-methylenedioxybenzylaminomethyl-1:2:3:4-tetrahydroquinoline, m.p. 53—54° (sparingly sol. sulphate, nitrate, phosphate, oxalate, perchlorate, picrate, mono-, m.p. 212—213°, and di-, m.p. 179—180° after softening at 171°, -hydrochloride). Similarly (I) and veratraldehyde afford a non-cryst. Schiff's base, hydrogenated to 6-methoxy-2-3':4'-dimethoxybenzylaminomethyl-1:2:3:4-tetrahydroquinoline (sparingly sol. sulphate, nitrate, phosphate, formate, oxalate, perchlorate, picrate; freely sol. acetate, citrate, tartrate; hydrochloride, m.p. 182—183° after softening at 179°). 1-Aminomethyltetrahydroisoquinoline and piperonal give a non-cryst. Schiff's base, hydrogenated to 1-3':4'-methylenedioxybenzylaminomethyl-1:2:3:4-tetrahydroisoquinoline [sparingly sol. sulphate, nitrate, hydrobromide, picrate, perchlorate, oxalate, and phosphate; freely sol. formate, acetate, tartrate, and citrate; dihydrochloride, m.p. 248—249° (decomp.)]. Non-cryst. 1-3':4'-dimethoxybenzylaminomethyl-1:2:3:4-tetrahydroisoquinoline gives a sparingly sol. oxalate, m.p. 197° (decomp.), picrate, perchlorate, sulphate, and hydriodide and a freely sol. dihydrochloride, m.p. 221° (decomp.), hydrobromide, nitrate, phosphate, acetate, tartrate, and citrate. Improved methods of obtaining 1-benzoyl-1:2-dihydroquinoline-2-nitrile and 2-benzamidomethyltetrahydroquinoline (II) are indicated. Reduction of 1-nitroso-2-benzamidomethyl-1:2:3:4-tetrahydroquinoline, m.p. 156° [picrate, m.p. 165° (decomp.)], which shows all the properties characteristic of a hydrazine and gives a benzylidene, m.p. 158—159°, piperonylidene, m.p. 184—185° after softening at 182°, and an α-phenylethylidene, m.p. 161—162°, derivative; (II) is formed as by-product and is sole product of the catalytic reduction. Hydrolysis of (II) with boiling conc. HCl gives 2-aminomethyltetrahydroquinoline (III) in 93—95% yield. Addition of nicotiny chloride in Et₂O or C₆H₆ to (III) gives 1-nicotinyl-2-nicotinamido-1:2:3:4-tetrahydroquinoline, m.p. 175—176°. 1-Veratroyl-2-veratramido-1:2:3:4-tetrahydroquinoline has m.p. 168°. Veratraldehyde and (III) give a non-cryst. product (picrate), hydrogenated (Ni in MeOH) to 2-3':4'-dimethoxybenzylaminomethyl-1:2:3:4-tetrahydroquinoline, m.p. 75° (hydrochloride, m.p. 191—192°; sulphate, m.p. 161.5°). Similarly condensation with piperonal followed by reduction leads to 2-3':4'-methylenedioxybenzyl-

aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline (hydrochloride, m.p. 213—214°; sulphate, m.p. 177—178°; phosphate, m.p. 204—205°). 1-Methyl-2-nicotinamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. 159—160°, gives a mono-, m.p. 223°, and di-hydrochloride, 1-Methyl-2-veratramidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. 161—162°, and its hydrochloride, m.p. 161—162°, are described. With piperonal and veratraldehyde 1-methyl-2-aminomethyltetrahydroquinoline gives non-cryst. Schiff's bases, reduced respectively to 1-methyl-2-3' : 4'-methylenedioxybenzylaminomethyl- (hydrochloride, m.p. 207—208°) and 1-methyl-2-3' : 4'-dimethoxybenzylaminomethyl- [perchlorate, m.p. 193° (decomp.)] -1 : 2 : 3 : 4-tetrahydroquinoline. H. W.

2-Aminomethyltetrahydroquinoline and its derivatives. H. VON BIDDER and H. RUPE (Helv. Chim. Acta, 1939, 22, 1268—1278).—2-Aminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline (I) (improved prep. from 2-cyano-1-benzoyl-1 : 2-dihydroquinoline; cf. A., 1939, II, 345) gives a monohydrochloride, m.p. 257°, dihydrochloride, b.p. 265° (decomp.), monohydrobromide, decomp. 235—236°, Ac derivative, m.p. 48.5—49.5°, CHPh compound, m.p. 75—76°, formate, m.p. 117.5—118.5°, and a very hygroscopic formyl derivative, b.p. 178—180°/10 mm., m.p. between 20° and 40° (perchlorate). Addition of CH₂Cl·CO₂Et to (I) in C₆H₆ affords the non-cryst. Et 2-tetrahydroquinolylmethylaminoacetate [normal oxalate, m.p. 169—170° (decomp.)]. Similarly, (I) and ClCO₂Et afford Et 2-tetrahydroquinolylmethylaminoformate, b.p. 120—125°/10 mm. (much decomp.) [hydrochloride, m.p. 135.5°; unstable perchlorate, m.p. 124°], readily converted into the iminazolone, CH₂< $\begin{smallmatrix} \text{CH}_2 & \text{CH} & \text{CH}_2 \\ & \text{C}_6\text{H}_4 & \text{N} \end{smallmatrix}$ —CO>NH, b.p. 245—247°/10 mm., m.p. 197°. (I) with (CH₃)₂O at 100° gives mono-, b.p. 232—235°/10 mm., m.p. 105.5—106.5°, and di-2-β-hydroxyethylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b.p. 235—245°/10 mm., m.p. 92—93° [Bz₂, m.p. 115—116°, and Bz₃ derivative, m.p. 95—96°, and its primary diorthophosphate, m.p. 151—152° (decomp.), and monohydrochloride, m.p. 100.5—103.5° (decomp.)]. 2-Benzamidomethyltetrahydroquinoline (II) and (CH₃)₂O at 110—120° afford 2-benzamidomethyl-1-β-hydroxyethyltetrahydroquinoline, m.p. 113—114.5° after softening at 110°. 1-Methyl-2-aminomethyltetrahydroquinoline (III) and (CH₃)₂O at 110° yield 1-methyldi-2-β-hydroxyethylaminomethyltetrahydroquinoline, b.p. 260—265°/12.5 mm., 177—179°/0.005 mm., which does not give cryst. salts. (III) gives a normal dicarbonate, m.p. 123—125°. Epichlorohydrin does not give useful results with (III) whereas it is converted by (II) at 100° into 1-benzamidomethyl-1-β-γ-oxidopropyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. 118—119°. CH₂Cl·COMe and CH₂Br·COPh react violently with (I) whereas (II) and CH₂Br·COPh give 1-phenacyl-2-benzamidomethyl-1 : 2 : 3 : 4-tetrahydroquinoline, m.p. 163°. 2-β-Hydroxy-β-methylamylaminomethyl-1 : 2 : 3 : 4-tetrahydroquinoline is a viscous, yellow liquid [hydrochloride, m.p. 171—173° (decomp.)].

H. W.

Condensation of arsenic halides with hydrohalides of pyridine and quinoline. P. P. POPOV (J. Gen. Chem. Russ., 1939, 9, 1264—1273).—

As halides form complexes when heated with the hydrohalides of C₅H₅N and quinoline in CHCl₃. The following are described : 2C₅H₅NHCl·AsCl₃·CHCl₃, deliquescent needles; C₅H₅NHBr·AsCl₃, microcryst. powder giving colourless needles of 3C₅H₅NHBr·2AsBr₃·CHCl₃ when crystallised from CHCl₃, and yellow needles of 2C₅H₅NHBr·AsBr₃·CHCl₃, which lose CHCl₃ when dried at 100° and when boiled with C₆H₆ give 5C₅H₅NHBr·2AsBr₃, a yellow powder; the reverse change can be brought about by boiling with CHCl₃; C₅H₅NHI₂·2AsI₃, small red crystals giving orange crystals of C₅H₅NH·AsI₃ when boiled with CHCl₃. C₆H₇NHCl·AsCl₃, needles, m.p. 122—123°; C₆H₇NHBr·AsBr₃, greenish-yellow crystals, m.p. 147—148°; C₆H₇NHI₂·2AsI₃, pale orange ppt. giving golden-yellow leaflets of C₆H₇NHI·AsI₃ when boiled with CHCl₃. All these complexes are hygroscopic, those containing I less than the others. When dissolved in H₂O they decompose, the whole of the halogen becoming ionic and the CHCl₃ being split off intact. The new compounds and the analogous Sb and Bi compounds can be classified into 5 groups and a scheme of formulation is suggested. G. A. R. K.

4-Amino-2-phenylquinoline derivatives. U. P. BASU and P. K. DAS-GUPTA (J. Indian Chem. Soc., 1939, 16, 301—304).—4-Amino-2-phenylquinoline (I) heated (12—24 hr.) with NEt₂·[CH₂]₂·Br or NEt₂·[CH₂]₃·Cl (II), K₂CO₃, and a trace of Cu powder in xylene gives respectively 4-(β-diethylaminooethyl)-, b.p. 272—276°/6 mm. (hydrochloride; picrate, m.p. 238—239°), and 4-(γ-diethylaminopropyl)-amino-2-phenylquinoline, b.p. 265—270°/6 mm. (picrate, m.p. 234°). 4-Chloro-2-phenylquinoline (III) with NEt₂·[CH₂]₄·NH₂ (IV), K₂CO₃, and Cu in C₅H₁₁·OH at 110—120°, or with NEt₂·[CH₂]₃·CHMe·NH₂ at 150—160°, gives respectively 4-(δ-diethylaminobutyl)- (picrate, m.p. 203°) and 4-(δ-diethylamino-α-methylbutyl)-aminoquinoline (picrate, m.p. 162°). 4-Amino-6-methoxy-2-phenylquinoline (V), new m.p. 159° (cf. John, A., 1931, 965), with (II) at 160—170° followed by addition of K₂CO₃ and steam-distillation gives 4-(γ-diethylaminopropyl)- (picrate, m.p. 185°), while 4-chloro-6-methoxy-2-phenylquinoline with (IV) gives 4-(δ-diethylaminobutyl)-amino-6-methoxy-2-phenylquinoline (picrate, m.p. 192°). With p-NH₂·C₆H₄·SO₂·NH₂ or p-NH₂·C₆H₄·SO₂·NEt₂ and a little Cu powder at 160—170°, (III) gives respectively 4-(p-sulphonamido)-, m.p. 250°, and 4-(p-sulphondieethylamido)-anilinoquinoline, m.p. 144°. With (I) in C₆H₆ at the b.p. or with (V) in NPhMe₂ at 150°, p-NHAc·C₆H₄·SO₂Cl gives 4-p'-acetamidobenzenesulphonamido-2-phenyl-, m.p. 297°, and -6-methoxy-2-phenylquinoline, m.p. 268°; these are respectively hydrolysed to the 4-p'-NH₂-compounds, m.p. 293° and 268°.

E. W. W.

8-Hydroxyquinoline derivatives.—See A., 1939, I, 625.

Action of nitric acid on polycyclic indole derivatives. XIII. Indeno-(2' : 3' : 2 : 3)-indole. N. M. BEYTS and S. G. P. PLANT (J.C.S., 1939, 1534—1536).—1-Acetylindeno-(2' : 3' : 2 : 3)-indole, m.p. 131°, is nitrated (HNO₃-AcOH) to a mixture of 3-nitro-2-acetoxy-1-acetyl-2 : 3-dihydroindeno-(2' : 3' : 2 : 3)-

indole, m.p. 177—180° (decomp.), and 6(?)-nitro-1-acetylindeno-(2':3':2:3)-indole, m.p. 275° (decomp.); the latter compound is not identical with 5-nitro-1-acetylindeno-(2':3':2:3)-indole, m.p. 247°, prepared by acetylating the 5-nitro-indeno-compound, m.p. 255°, the product of the Fischer reaction on β -hydrindone-*p*-nitrophenylhydrazone. 1-Benzoylindeno-(2':3':2:3)-indole, m.p. 169—170°, does not give a similar additive product on nitration. The β -naphthylhydrazone of β -hydrindone, m.p. 176° (decomp.), with AcOH gives indeno-(2':3':2:1)- β -naphthindole, m.p. 208—209°, the 3-Ac derivative, m.p. 185°, of which with HNO₃-AcOH affords only ?-nitro-3-acetylindeno-(2':3':2:1)- β -naphthindole, m.p. 265° (decomp.), indicating that additive tendency is diminished by the presence of the extra C₆H₅ nucleus.

F. R. S.

Meso-derivatives of acridine. XII. 5-Chloro-acridine and acridol. N. S. DROZDOV. XIII. Preparation and anti-malarial action of substituted 5-aminoacridines. O. M. TSCHERNITZOV and N. S. DROZDOV (J. Gen. Chem. Russ., 1939, 9, 1373—1375, 1435—1440).—XII. 5-Chloro- and 5-chloro-2-methyl-acridine gradually decompose in air and light, to give substances of the type $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} C_6H_4 \cdot C_6H_4 \begin{smallmatrix} CCl \\ \diagup \quad \diagdown \\ N \end{smallmatrix} C_6H_4$, which yield acridone when distilled. To this are due the reports made by a no. of authors to the effect that acridone or acridol are obtained by distillation of 5-chloroacridine derivatives.

XIII. 3-Dimethylamino-5-phenoxyacridine in PhOH and γ -piperidino- β -hydroxypropylamine, heated at 100° for 1 hr., yield 3-dimethylamino-5-(γ -piperidino- β -hydroxypropyl)aminoacridine, m.p. 213—215°. The following are prepared analogously: 8-chloro-3-dimethylamino-5-(γ -piperidino- β -hydroxypropyl)-, an oil, 8-chloro-3-dimethylamino-5-(γ -diethylamino- β -hydroxypropyl)-, m.p. 108—109°, 3-dimethylamino-5-(8-diethylamino- α -methylbutyl)-, an oil, 8-chloro-3-dimethylamino-5-(8-diethylamino- α -methylbutyl)-aminoacridine (I), an oil, 5-(8-diethylamino- α -methylbutyl)amino-3-methoxy-, an oil, 2-chloro-5-(γ -piperidino- β -hydroxypropyl)amino-7-methoxy- (II), m.p. 130—131.5° [hydrochloride, m.p. 255° (decomp.)], 3-nitro-9-(γ -piperidino- β -hydroxypropyl)amino-7-methoxy-, m.p. 170—171°, 4-nitro-5-methylamino-1-methoxy-acridine, m.p. 211—213°. 2:5-Dichloro-7-methoxy-acridine, sulphanilamide, and PhOH (3 hr. at 100°) afford 4-(2'-chloro-7'-methoxy-5'-acridyl)aminobenzene-sulphonamide, not melting at 300°. (I) and (II) have a pronounced schizotropic action in avian malaria.

R. T.

Acridine derivatives as antimalarials. IV. S. J. DAS-GUPTA (J. Indian Chem. Soc., 1939, 16, 364—368; cf. A., 1939, I, 282).—5:2:1-SO₂Cl·C₆H₃Cl·CO₂H (I) and *p*-NH₂·C₆H₄·SO₂·NH₂ (2 mols.) give 2-chloro-5-*p*'-(amidodisulphonyl)anilidosulphonylbenzoic acid, m.p. 240°, which with *p*-OMe·C₆H₄·NH₂ and K₂CO₃ in C₅H₁₁·OH gives 4-*p*'-(amidodisulphonyl)anilidosulphonyl-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 246°, converted by POCl₃ at 100° into 5-chloro-3-*p*-(amidodisulphonyl)anilidosulphonyl-, m.p. 212—215°, which in PhOH with NH₂·CHMe·[CH₂]₃·NEt₂ and NH₂·[CH₂]₄·NEt₂

at 100° gives 3-*p*-(amidodisulphonyl)anilidosulphonyl-5-(8-diethylamino- α -methyl-*n*-butylamino)-, m.p. 254—256°, and -5-(8-diethylamino-*n*-butylamino)-7-methoxy-acridine, m.p. 220—222°, respectively. Similarly (I) and *p*-NH₂·C₆H₄·SO₂·NEt₂ give 2-chloro-5-*p*'-(diethylamidodisulphonyl)anilidosulphonylbenzoic acid, m.p. 194—195°, whence 4-*p*'-(diethylamidodisulphonyl)anilidosulphonyl-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 202—203°, 5-chloro-3-*p*-(diethylamidodisulphonyl)anilidosulphonyl-, m.p. 187—189°, and 3-*p*-(diethylamidodisulphonyl)anilidosulphonyl-5-(8-diethylamino- α -methyl-*n*-butylamino)-, m.p. ~160°, -5-(8-diethylamino-*n*-butylamino)-, m.p. ~130°, and -5-(γ -diethylamino-*n*-propyl)-7-methoxyacridine, m.p. ~200°, are obtained. *p*-NH₂·C₆H₄·SO₂·NEt₂ and *p*-NHAc·C₆H₄·SO₂Cl give the Ac derivative, m.p. 228°, of *p*'-aminobenzene-sulphonanilido-*p*-sulphon-diethylamide, m.p. 176°, which with 2:5-dichloro-7-methoxy- or -7-methyl-acridine gives respectively 2-chloro-5-*p*'-(diethylamidodisulphonyl)anilido-*p*-sulphonylanilino-7-methoxy-, m.p. 160—161°, and -7-methyl-acridine, m.p. 133—134°. E. W. W.

Action of ethyl acetoacetate on 2-aminopyridine. S. N. CHITRIK (J. Gen. Chem. Russ., 1939, 9, 1109—1117).—2-Aminopyridine and CH₃Ac·CO₂Et, heated at 150—160° (4—5 hr.), yield 6-methyl-1:2-benz-4-pyrimidone (II), m.p. 122° [+H₂O, m.p. 105—107°; +1½H₂O, m.p. 84°; platinichloride, m.p. 229° (decomp.); hydrochloride, m.p. 315°; picrate, m.p. 177° (decomp.); methiodide, not melting at 280°; compound with maleic anhydride, m.p. 135—136°; 5-NO₂-derivative, m.p. 184°]. At 100° (4 hr.) the product is 2-acetoacetamidopyridine, m.p. 113° [methiodide, m.p. 133—134° (decomp.)], which with H₂SO₄ (24 hr. at room temp.) gives (I). At 130° the product is the 2-pyridylamide of β -2-pyridylaminocrotonic acid, m.p. 166°. R. T.

Oxidation products of indole. C. TOFFOLI (R. Ist. San. Pubbl., 1939, 2, 565—572).—Mg 2-methylindolyl bromide (I) and O₂ give a yellow, cryst. product (II), C₁₃H₁₆ON₂, m.p. 208° (cf. Oddo, A., 1921, i, 127), and di-(2-methyl-3-indolyl), m.p. 237—238°, also afforded by (I) with Mg Et acetoacetate. Mg indolyl bromide and O₂ give a small amount of a product, m.p. 255—260° (decomp.). Spontaneous oxidation of 2-methylindole also affords (II) and a product (2-ketoindole ?), m.p. 120°.

F. O. H.

Molecular combination of iminomethenyl compounds. C. TOFFOLI (R. Ist. San. Pubbl., 1939, 2, 677—708).—The yellow compound (I), m.p. 208°, of Oddo (cf. preceding abstract) is considered to be di-(2-methyl-3-indolyl) oxide; if this is true, it should be colourless. Various reactions of (I) with alkalis, NaHSO₃, NH₂OH, etc. are always attended by formation of 2-methylindole. These and parallel reactions indicate that (I) is formed not by a reaction involving an active H, viz., —CH:N— + HR \rightarrow —CHR·NH—, but by a mol. combination of the type —CH:N···H—R. Such a concept is applicable to, e.g., theobromine and indigotin. F. O. H.

Acids derived from various heterocyclic types.—See B., 1939, 1104.

Canavanine picrolonate; deaminocanavanine picrate, decomp. 216—217°, and flavianate, decomp. 225—226°.—See A., 1939, III, 1004, 1005.

Constitution of uric acid riboside.—See A., 1939, III, 986.

Isolation and structure of bonelline, the green pigment of *Bonellia viridis*. E. LEDERER (Compt. rend., 1939, 209, 528—530).—Bonelline (I) (prep. described), m.p. >300°, exhibits dichroism in conc. solution in org. solvents, and forms with CH_2N_2 a OMe-derivative which gives complex Cu, Fe, and Zn salts. The absorption spectra of (I) and mesopyrrochlorin (II) in dioxan and 12% HCl and the two fluorescence spectra are nearly identical (cf. Stern and Molvig, A., 1937, I, 165). (I) is probably $\text{C}_{34}\text{H}_{36}\text{O}_4\text{N}_4 \pm \text{H}_2$, which is 6- γ -dihydroxymesopyrrochlorin (cf. Herrlo, *et al.*, A., 1936, 1272), the OH groups being remnants of the isocyclic ring in α -chlorophyll. J. L. D.

Melanin and its precursors. I. W. L. C. VEER (Rec. trav. chim., 1939, 58, 949—955).—Tyrosine in H_2O is oxidised with O_2 + tyrosinase (p_{H} 6—6.5) to give an aq. solution (I) of "red substance" (II) (cf. Raper, A., 1927, 278). (I) and $\text{NHPh}\cdot\text{NH}_2$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, or $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$, in 30% aq. AcOH , give the corresponding monohydrazones, m.p. $\sim 168^\circ$ (decomp.) (indefinite) ($+\text{H}_2\text{O}$), m.p. $\sim 190^\circ$ (decomp.) (indefinite) ($+\text{H}_2\text{O}$), or m.p. $\sim 174^\circ$ (decomp.) ($+2\text{H}_2\text{O}$), respectively. (I) and NH_2OH , $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, or $2:4:1\text{-(NO}_2)_3\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ do not react. Results support the constitution of (II) given by Raper (*loc. cit.*); it may be important as an anti-pernicious anaemia principle. A. T. P.

Synthesis of 4-methyl-5- β -hydroxyethylthiazole and its homologues. A. G. PESINA (J. Gen. Chem. Russ., 1939, 9, 804—813).— $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{CHAcCl}$ (I) is synthesised: (i) $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ and $(\text{CH}_2\text{Br})_2$ give *Et* γ -bromo- α -acetylbutyrate, b.p. 67—75°/5—6 mm., converted by SO_2Cl_2 at 0° into *Et* α -chloro- γ -bromo- α -acetyl butyrate, b.p. 119—123°/7—9 mm., yielding (I) on hydrolysis with $\text{AcOH-H}_2\text{SO}_4$, and (ii) $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ and $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{Br}$ yield *Et* γ -hydroxy- α -acetylbutyrate, b.p. 75—80°/20—22 mm., converted by SO_2Cl_2 into *Et* α -chloro- γ -hydroxy- α -acetylbutyrate, b.p. 95—103°/12—14 mm., which gives (I) on hydrolysis with $\text{AcOH-H}_2\text{SO}_4$. (I) and $\text{NH}\cdot\text{CH}\cdot\text{SH}$ yield 4-methyl-5- β -hydroxyethylthiazole (A., 1936, 1394). The synthesis of this compound is described: 2:4-dimethyl-5- β -hydroxyethylthiazole, b.p. 130—131°/7—8 mm. (picrolonate, m.p. 139—140°); 4-methyl-2-ethyl-5- β -hydroxyethylthiazole, b.p. 133—136°/3—5 mm. (picrolonate, m.p. 149—151°); 4-methyl-2-propyl-5- β -hydroxyethylthiazole, b.p. 140—142°/3—5 mm., and 4-methyl-5- β -hydroxyethylthiazole (picrolonate, m.p. 196—197°). V. A. P.

Reactions in the thiazole series. II. Reaction of 1-chlorobenzthiazole with thiocarbamide in aqueous media. G. W. WATT (J. Org. Chem., 1939, 4, 436—441).—Protracted action of 1-chlorobenzthiazole and $\text{CS}(\text{NH}_2)_2$ in H_2O at room temp. gives 1-thiolbenzthiazole (I), m.p. 179.2—180° corr.), and 1:1'-dibenzthiazolyl sulphide (II), m.p.

98.7—99.1° (corr.). The yields of (I) and (II) are decreased with decrease in concn.; at any particular concn. the yield increases with increased time of action and the rate at which these reactions approach completion is increased by the presence of either (I) or (II). The formation of (II) is dependent on the formation and ionisation of an intermediate additive compound. H. W.

High mol. wt. fatty acid derivatives. I. Characterisation of acids. H. GILMAN and G. M. FORD (Iowa State Coll. J. Sci., 1939, 13, 135—147).—Carbazole (0.01 mol.) with the acid chloride (0.01 mol.) (prepared from the acid and SOCl_2) at 100—150° until no more HCl is evolved affords the *N*-acylcarbazole. The following are prepared: *N*-lauryl-, m.p. 78—79°, -myristyl-, m.p. 81—82°, -palmityl-, m.p. 85—86°, -oleyl-, an oil, and -stearyl-carbazole, m.p. 91—92°. The following *N*-acylphenothiazines are prepared similarly: *N*-lauryl-, m.p. 70°, -myristyl-, m.p. 75°, -palmityl-, m.p. 80°, -oleyl-, an oil, and -stearyl-phenothiazine, m.p. 86°. Equiv. amounts of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ and the acid chloride at 100—125°/2 hr. afford *N*-lauryl-, m.p. 83—84°, -myristyl-, m.p. 89—90°, -palmityl-, m.p. 93—94°, -oleyl-, an oil, and -stearyl-*p*-toluenesulphonamide, m.p. 98—99°. $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ with the appropriate acid and Na_2CO_3 affords *p*-phenylphenacyl myristate, m.p. 90°, palmitate, m.p. 94°, and stearate, m.p. 97° (lit., 91°). $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ with the acid chloride affords laur-, m.p. 78°, myrist-, m.p. 84°, palmit-, m.p. 93°, and stear-*p*-nitroanilide, m.p. 96°. The Na derivative of saccharin (0.01 mol.) with the acid chloride (0.01 mol.) in boiling CHCl_3 /3 hr. gives *N*-lauryl-, m.p. 88—89°, -myristyl-, m.p. 90—91°, -palmityl-, m.p. 90°, -oleyl-, an oil, and -stearyl-saccharin, m.p. 95°. The following are prepared according to Cerezo and Olay's directions (A., 1936, 1251): lauryl-, m.p. 110—111°, myristyl-, m.p. 118°, palmityl-, m.p. 120—121°, and oleyl 2:4-dinitrophenylhydrazide. Equimol. amounts of 2-nitro-*p*-toluidine and the acid chloride at 100—150°/3 hr. give *N*-lauryl-, m.p. 62—63°, -myristyl-, m.p. 73—74°, -palmityl-, m.p. 78—79°, and -stearyl-2-nitro-*p*-toluidide, m.p. 85°. Similarly, $\text{Hg}(p\text{-C}_6\text{H}_4\text{Me})_2$ and the acid chloride in boiling xylene/8 hr. afford *Hg* *p*-tolyl laurate, m.p. 93—94°, myristate, m.p. 95—96°, palmitate, m.p. 99°, oleate, an oil, and stearate, m.p. 102—103°. The following are prepared similarly: *Hg* *Ph* laurate, m.p. 82°, myristate, m.p. 86°, palmitate, m.p. 93°, oleate, an oil, and stearate, m.p. 95°. Equimol. amounts of PbPh_3 and the acid in boiling xylene/10 hr. give *Pb* *Ph* laurate, m.p. 91°, myristate, m.p. 102—103°, palmitate, m.p. 110°, and stearate, m.p. 112°. SnPh_4 and stearic acid do not react even in presence of SiO_2 gel or when heated under pressure. Equimol. amounts of $\text{CO}(\text{NH}_2)_2$ and the acid chloride in boiling dry $\text{C}_5\text{H}_5\text{N}$ afford (cf. Stendal, A., 1933, 806; Jacobson, A., 1936, 1495): lauryl-, m.p. 182°, myristyl-, m.p. 178°, and palmityl-carbamide, m.p. 175°. Lauryl-, m.p. 138°, myristyl-, m.p. 135°, palmityl-, m.p. 135—136°, stearyl-, m.p. 133°, and oleyl-thiocarbamide, m.p. 112—113°, are prepared similarly. Et stearate with $\text{CS}(\text{NH}_2)_2$ in 25% $\text{NaOEt-C}_5\text{H}_5\text{N}$ gives distearylthiocarbamide, m.p. 100°. Equimol. amounts of the acids and *p*-xenylamine (I) at

135—140°/5 hr. (sealed tube) or of the acid chloride and (I) at 150—200°/5 hr. (sealed tube) afford (cf. Kimura and Nihayashi, A., 1936, 53) *laur*-, m.p. 146°, *myrist*-, m.p. 143°, *palmit*-, m.p. 142°, and *stear*-*p*-phenylanilide, m.p. 143°. 4-*Lauryl*-, m.p. 101—102°, -*myristyl*-, m.p. 102—103°, -*palmityl*-, m.p. 103—104°, and -*stearyl-diphenyl*-, m.p. 106—107°, are prepared by the Friedel-Crafts reaction in CS₂. Carbazole (0.005 mol.), the appropriate acid chloride (0.01 mol.), and AlCl₃ (0.02 mol.) in PhNO₂ yield 3:6-*dilauryl*-, m.p. 176°, -*dimyristyl*-, m.p. 169°, and -*dipalmityl*-carbazole, m.p. 162°. *p*-NH₂·C₆H₄·CO₂H (0.01 mol.) and acid chloride (0.01 mol.) in boiling C₅H₅N/5 hr. give *p-laur*-, m.p. 227—228°, -*myrist*-, m.p. 224—225°, -*palmit*-, m.p. 226—227°, and -*stear*-amidobenzoic acid, m.p. 221°. *N*-*Palmityl*- and -*stearyl-anthranilic acid*, m.p. 100° and 113°, respectively, are prepared similarly by refluxing in CHCl₃. Equimol. amounts of 2-aminodiphenylene oxide and acid chloride at 125—160°/5 hr. give 2-*palmit*-, m.p. 130°, and -*stear*-amidodiphenylene oxide, m.p. 134°. Benzidine (0.005 mol.) with the acid chloride (0.01 mol.) in boiling dry C₅H₅N/5 hr. gives *dilauryl*-, m.p. 248°, *dimyristyl*-, m.p. 241—242°, *dipalmityl*-, m.p. 233°, and *distearyl-benzidine*, m.p. 232°. Equimol. amounts of 3-*stearyl*carbazole (II) and *stearyl* chloride at 150—200° give 3:*N*-*distearyl*carbazole (III), m.p. 86—87°. A Friedel-Crafts reaction on the same reactants gives 3:6-*distearyl*carbazole. (III) with boiling EtOH-HCl/4 hr. gives (II) and stearic acid. J. L. D.

Alkaloids of *Mitragyna rotundifolia*. I. G. BARGER, E. DYER, and L. J. SARGENT (J. Org. Chem., 1939, 4, 418—427).—Percolation of the air-dried leaves of *M. rotundifolia* with 95% EtOH leads to *rhynchophylline* (I) and *rotundifoline* (II). (I) is identical with the mitrinermine of Raymond-Hamet *et al.* (A., 1935, 366) and the alkaloid of *Ouonparia rhynchophylla*. (I), C₂₂H₂₈O₄N₂, m.p. 208—209°, [α]_D²⁵ -14.5° in CHCl₃, contains 2 OMe, one of which is present as CO₂Me, but no CH₂O₂. One N is *tert.* and basic whereas the other belongs to an indole ring. NMe is absent. The function of the fourth O is unknown since (I) gives negative tests for OH, enol, or CO. The active H (Zerevitinov) may be assigned to NH. The suggestion that (I) is a OMe-derivative of yohimbine does not appear to be supported by chemical or optical evidence. (I) is hydrolysed to amorphous *rhynchophyllic acid*, slow decomp. >150° after softening at 140°, which, when distilled with CaO, gives an unidentifiable oil and a neutral substance, C₁₀H₉ON, m.p. 182—184° after softening at 180°, which dissolves in boiling alkali and gives a substance yielding a positive Ehrlich action when distilled with Zn dust; it is possibly a methylcarbostyryl. Degradation of (I) by heating with soda-lime gives a mixture of oxygenated indoles, NH₃, and a base, C₈H₉ON or C₈H₁₁ON (*picrate*, m.p. 123—125° after softening at 115°), which resembles C₅H₅N. CO₂ is evolved when (I) is boiled with 30% H₂SO₄ and a residue resembling that derived from mitragynine is obtained. (II), m.p. 233—234°, [α]_D²⁵ +124° in CHCl₃, is C₂₂H₂₆O₅N₂. It contains 2 OMe (one present in CO₂Me), but no CH₂O₂ or NMe. It contains 1.4 active H, part of

which may be ascribed to an enolic OH since a deep red colour is produced with FeCl₃ in non-hydroxylic solvents. The nature of the remaining two O is uncertain since (II) does not give definite products of acetylation and does not yield a semicarbazone. One of the N is basic and *tert.*; the other is a member of an indole ring. (II) is hydrolysed to the amorphous, amphoteric *rotundifolic acid*, C₂₁H₂₄O₅N₂, which softens at 160°, effervesces at >165°, and becomes brown at 170°. Decarboxylation of (II) by CaO leads to the base, C₂₀H₂₄O₃N₂, m.p. 200—202° after softening at 198°. When heated with soda-lime (II) gives a mixture of indoles, NH₃, and bases resembling C₅H₅N. CO₂ is eliminated when (II) is boiled with 30% H₂SO₄ and the residue is similar to that derived from (I). Dehydrogenation of (II) by *So* gives a mixture from which the base, C₉H₁₃N (*picrate*, m.p. 134—135°), is isolated; it is optically inactive, does not give a NO-derivative, but yields a non-cryst. *methiodide*. A quantity of amorphous alkaloid, the composition of which is similar to that of (I) and (II), was isolated. Its corresponding acid yields the substances C₁₀H₉ON and C₉H₁₃N. H. W.

Crystalline alkaloid of the Rubiaceae described by Schumann as *Adina rubrostipulata*. RAYMOND-HAMET (Bull. Sci. Pharmacol., 1939, 41, 327—336).—Rubradinine (Denis, A., 1937, II, 266) is identical with mitraphylline (*ibid.*, 217). R. T.

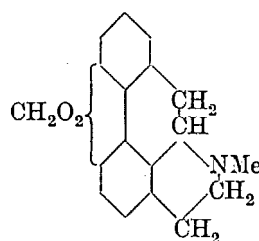
Synthesis of the alkaloid pilosinine. A. M. POLJAKOVA, V. A. PREOBRASHENSKI, and N. A. PREOBRASHENSKI (J. Gen. Chem. Russ., 1939, 9, 1402—1409).—(CH₂·CO₂Et)₂ and HCO₂Et condensed in NaOMe-MeOH (2 days at 0°, then 2 days at room temp.) yield Et₂ formylsuccinate, reduced (Al-Hg) to Et₂ itaconate, converted by distillation into *Et pilosinate*, b.p. 273—276°, hydrolysed to *pilosininic acid*, CO<CH₂>CH·CO₂H, m.p. 64—65°, the *chloride*, b.p. 107°/12 mm., of which is treated with CH₂N₂. The resulting pilosinyl diazomethyl ketone, shaken with Ag₂O in EtOH, yields *Et homopilosinate*, b.p. 161°/15 mm., hydrolysed to *homopilosininic acid*, m.p. 86.5—87.5°, the *chloride*, b.p. 126°/0.2 mm., of which is treated with CH₂N₂, and the homopilosinyl diazomethyl ketone thus obtained is converted into *homopilosinyl acetoxymethyl ketone* (I), b.p. 168°/0.5 mm., by the action of AcOH at 70°, and into the *chloromethyl ketone* (II), b.p. 163°/0.7 mm., by saturation of its Et₂O solution with HCl. (II) in EtOH and K phthalimide (8 hr. at 100°) give *homopilosinyl phthalimidomethyl ketone*, m.p. 146—147°. This, heated with 1:1 HCl (8 hr. at the b.p.), affords *homopilosinyl aminomethyl ketone* (*hydrochloride*, m.p. 140—143°), which with aq. KCNS (8 hr. at 100°) gives 2-*thiopilosinidine*, m.p. 202.5—203°, and this is converted by boiling with aq. FeCl₃ into pilosinidine (III) (*nitrate*, m.p. 117—118°), from which pilosinine is prepared by treatment successively with MeI and KOH. (III) is also prepared by shaking (I) with aq. Cu(OAc)₂, aq. CH₂O, and aq. NH₃, and then passing H₂S at 100° (Weidenhagen reaction). R. T.

Constitution and synthesis of the alkaloid anonaine. G. BARGER and G. WEITNAUER (Helv.

Chim. Acta, 1939, **22**, 1036—1047; cf. Santos, A., 1931, 242).—Anonaine (I), m.p. 122—123°, $[\alpha]_D^{20} -52^\circ$ in CHCl_3 , obtained by percolating the bark of *Anona reticulata* with 95% EtOH, is $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$. The hydrochloride has m.p. 277.5° (decomp.). It is a sec. non-phenolic base since it gives the basic *N*-methyl-anonaine [hydriodide, m.p. 246—247° (decomp.)], a neutral *NO*-derivative, m.p. 229—230°, and an *Ac* compound, m.p. 229—230°. It contains 1 active H (Zerevitinov) and CH_2O_2 but not *NMe*, *OMe*, CO_2H , or *CO*. *MeI* and (I) in H_2O afford the quaternary iodide, $\text{C}_{19}\text{H}_{20}\text{O}_2\text{NI}$, m.p. 217°, transformed by $\text{KOH-EtOH-H}_2\text{O}$ into the methine base, m.p. 87—90°, the methiodide, m.p. 270.5° (decomp.), of which is converted into methylenedioxyvinylphenanthrene (II), m.p. 87°. This is oxidised to methylenedioxyphenanthrenecarboxylic acid, sublimes at 240° (partial decomp.), which is decarboxylated by *Cu* chromite in quinoline to methylenedioxyphenanthrene [picrate, m.p. 168° (decomp.)]. $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{COCl}$ and homopiperonylamine in C_6H_6 afford *o*-nitrophenylacet- β -3 : 4-methylenedioxyphenylethylamide, m.p. 119°, cyclised by POCl_3 in CHCl_3 at room temp. to 6 : 7-methylenedioxy-1 : *o'*-nitrobenzyl-3 : 4-dihydroisoquinoline (III), m.p. 165°. This is reduced (*Zn* dust and *HCl*) to the corresponding, non-cryst. *NH*₂-compound (dihydrochloride, m.p. 257°). This is diazotised and reduced to *dl*-anonaine, m.p. 285° (decomp.) (*Ac* derivative, m.p. 217°). The synthetic product is degraded (Hoffmann) in the same manner at (I), thus giving (II). *MeI* and (III) at 100° afford 6 : 7-methylenedioxy-1-*o'*-nitrobenzyl-3 : 4-dihydroisoquinoline methiodide, m.p. 243° (decomp.), converted by *Zn* dust and *HCl* at 100° into 6 : 7-methylenedioxy-1-*o'*-aminobenzyl-2-methyltetrahydroisoquinoline [dihydrochloride, m.p. 259—260° (decomp.)], which when diazotised and reduced gives *dl*-2-methyl-anonaine [hydriodide, m.p. 244° (decomp.)]; methiodide, m.p. 210—211°. H. W.

Alkaloids of *Roemeria refracta*, D.C. III.

Alkaloids of plants of the Papaveraceæ family. R. A. KONOVALOVA, S. JUNUSOV, and A. P. OREKHOV (J. Gen. Chem. Russ., 1939, **9**, 1356—1364).—The plant contains *l*-ephedrine, *d*- ψ -ephedrine, and roemerine, $\text{C}_{18}\text{H}_{17}\text{O}_5\text{N}$, m.p. 101—102.5° (hydrochloride, m.p. 262—263°; picrate, m.p. 195—196°), the methiodide, m.p. 215—216°, of which gives (by the Hofmann degradation) *de-N*-methylroemerine, m.p. 73—74°; the methiodide, m.p. 274—275°, of this, heated with KOH-EtOH , gives a product,



This is oxidised (KMnO_4) to an acid, $\text{C}_{16}\text{H}_{10}\text{O}_4$, m.p. 264°, which, when heated with $\text{Cu-Cr}_2\text{O}_3$, yields CO_2 and a methylenedioxyphenanthrene, m.p. 84—85° (picrate, m.p. 167—168°; Br_2 -derivative, m.p. 196—197°).

Roemerine (annexed structure) yield phenanthrene when distilled with *Zn* dust. R. T.

Dichloro-substituted phenylarsinic acids and their derivatives. G. I. BRAZ and I. V. TUTURIN

(J. Gen. Chem. Russ., 1939, **9**, 992—995).—2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$ in *AcOH* is diazotised in presence of AsCl_3 and *CuCl*, and the solution is heated at 100°, yielding 2 : 5-dichlorophenylarsinic acid, not melting at 250°, whence is obtained 2 : 5-dichlorophenyldichloroarsine, m.p. 56—57°. 2 : 4- and 3 : 4-Dichlorophenylarsinic acid, both not melting at 250°, and 2 : 4-, b.p. 167—168°/12 mm., and 3 : 4-dichlorophenyldichloroarsine, b.p. 175—176°/12 mm., are described. R. T.

Certain side-chain substituted derivatives of *p*-tolylarsinic acid. S. M. SCHERLIN, G. I. BRAZ, A. J. JAKUBOVITSCH, and A. I. KONOVALTSCHIK (J. Gen. Chem. Russ., 1939, **9**, 985—991).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ in H_2SO_4 and AsCl_3 is diazotised, and the product is heated with *CuCl*, yielding 4-hydroxymethylphenylarsinic acid, m.p. 165—171° (decomp.), which is converted into 4-hydroxymethylphenyldichloroarsine (I), an oil, and 4-hydroxymethylphenylarsine oxide, sinters at 260°, decomp. 264—265°. (I) in C_6H_6 and PCl_3 afford 4-chloromethylphenyldichloroarsine, m.p. 29—30°, converted by aq. H_2O_2 at room temp. into 4-chloromethylphenylarsinic acid. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ in *MeOH* is similarly converted into 4-carboxymethylphenyldichloroarsine (II), m.p. 89—90°, and 4-cyanomethylphenyldichloroarsine (III), m.p. 56—57°. This treated successively with NaHCO_3 and H_2O_2 , affords 4-cyanomethylphenylarsinic acid (IV), not melting at 280°. (IV) in *HCl* and SO_2 give (III), converted into the oxide, sinters at 216°, m.p. 218—220° (decomp.), by aq. NaHCO_3 . (IV) in conc. *HCl* and SO_2 afford the amide, m.p. 143—145°, of 4-carboxymethylphenyldichloroarsine, m.p. 107.5—109°. R. T.

Introduction of arsenic into the aromatic nucleus by means of mercury compounds. C. D. NENITZESCU, D. A. ISĂCESCU, and C. GRUDESCU (Bul. Soc. Chim. România, 1938, **20**, 135—138).— HgPhCl (2 mols.) and AsCl_3 (1 mol.) at 110° give 61% of AsPh_2Cl and 8% of AsPhCl_2 , separated by light petroleum. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{HgCl}$ (78) and AsCl_3 (60 g.) at 110° give $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{AsCl}_2$ (29 g.), converted by boiling aq. Cl_2 into $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{AsO}_3\text{H}_2$ (63%), which with NaNO_3 in H_2SO_4 gives the 3- NO_2 -acid and thence by 40% *KOH* at 100° 65% of 3 : 4 : 1- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{AsO}_3\text{H}_2$. R. S. C.

Mercuration of benzene and chlorobenzene. C. D. NENITZESCU, D. A. ISĂCESCU, and C. GRUDESCU (Bul. Soc. Chim. România, 1938, **20**, 127—134).—92% of $\text{HgPh}\cdot\text{OAc}$ is obtained by heating $\text{Hg}(\text{OAc})_2$ (1 mol.) in C_6H_6 (35 mols.) and *AcOH* (20 mols.) at 100° for 9 hr. Other mixtures give lower yields. $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{Hg}\cdot\text{OAc}$, similarly obtained in 50% yield, with aq. *Br* gives $p\text{-C}_6\text{H}_4\text{ClBr}$, and with *NaCl* in *AcOH* gives $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{HgCl}$, m.p. 240°. $\text{HgPh}\cdot\text{OAc}$ and $\text{Hg}(\text{OAc})_2$ are separated by the solubilities in C_6H_6 [1.6 g. of $\text{HgPh}\cdot\text{OAc}$ compared with 0.008 g. of $\text{Hg}(\text{OAc})_2$ per 100 c.c.]. R. S. C.

Mercury derivatives of phenacetin. M. RAGNO (Annali Chim. Appl., 1939, **29**, 414—418; cf. A., 1939, III, 396).— $\text{Hg}(\text{OAc})_2$ and phenacetin give 2-mercurophenacetin acetate, $\text{C}_{12}\text{H}_{15}\text{O}_4\text{NHg}$, m.p. 169—170° (decomp.), converted by *NaI* and *KOH* into the

corresponding *bromide*, m.p. 225°, and *hydrate*, m.p. 255—258° (decomp.), respectively, and, by aq. EtOH—Na₂S₂O₄, into 2-mercuridiphenacetin, C₂₀H₂₁O₄N₂Hg, decomp. 245°.

F. O. H.

Reaction between mercury diphenyl and mono-basic organic acids. M. M. KOTON (J. Gen. Chem. Russ., 1939, 9, 912—916).—HgPh₂ reacts with monobasic org. acids as follows: $\text{HgPh}_2 + \text{R}\cdot\text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_5 + \text{R}\cdot\text{CO}_2\text{HgPh}$. The following are described: Hg Ph formate, m.p. 135—138° (lit. m.p. 171°), acetate, propionate, m.p. 80—81° (lit. m.p. 145—165°), lactate, m.p. 154—155°, *n*-butyrate, m.p. 91°, α -hydroxybutyrate, m.p. 159°, hexoate, m.p. 82—83°, stearate, m.p. 90—92°, benzoate, m.p. 97—98°, and salicylate, m.p. 200°.

V. A. P.

Decomposition of iodonium salts. Reactions with mercury, tellurium, and antimony. R. B. SANDIN, F. T. McCURE, and F. IRWIN (J. Amer. Chem. Soc., 1939, 61, 2944—2946).—IR₃Cl (R = Ph or *p*-C₆H₄Me) and Hg in boiling Pr^oOH or H₂O give HgRCl. Similarly, IR₃Cl (R as before) and Te in boiling Pr^oOH or H₂O—EtOH—H₂S at room temp. give TeR₂, isolated as TeR₂Br₂. Heating IPh₂Cl and Te alone gives TePh₂Cl₂. IPh₂Cl, Na₂S, and Sb in Et₂O—H₂O at room temp. give (SbPh₃)₂S. Probably some at least of the IR₃Cl decomposes by a non-ionic mechanism, the octet of the I expanding to absorb the Cl and form a complex which then decomposes to PhI, Ph, and Cl.

R. S. C.

Reaction between triphenylbenzylphosphonium bromide and sodium. L. N. PARFENTEV and A. A. SCHAMSHURIN (J. Gen. Chem. Russ., 1939, 9, 865—867).—Na reacts with PPh₃Br·CH₂Ph with elimination of HBr to give PPh₃:CHPh, identified by hydrolysis to PPh₃O and PhMe.

V. A. P.

Micro-gas-analytical determination of the nitrogen content of organic compounds. H. GYSEL (Helv. Chim. Acta, 1939, 22, 1088—1095).—The front portion of the "supremax" tube contains wire-form CuO and three spirals of reduced Cu gauze. It is heated electrically by a fixed furnace at 720—730°. The back portion of the tube contains the substance mixed in a porcelain boat with CuO and PbCrO₄; it is followed by a Cu gauze. This portion of the tube is heated by a movable furnace operated at 800—810°. By means of a thermo-element it is possible to obtain a graph of the relation between temp. and distance between the fixed and movable furnaces and hence to regulate suitably the temp. to which the substance is exposed. The liberated N₂ is measured. Arrangement is made so that CO₂ can be passed through the tube in either direction, thus allowing fresh boats to be introduced during series analyses without infiltration of air or necessity of altering the heating by the fixed furnace. A complete analysis can be made in 35—45 min. and the error is $\pm 0.2\%$.

H. W.

Potentiometric studies in oxidation-reduction reactions. VI. Iodometric determination of organic acids. VII. Determination of aromatic compounds with potassium chlorate. B. SINGH and S. SINGH (J. Indian Chem. Soc., 1939, 16,

343—345; 346—348).—VI. H₂C₂O₄, tartaric, citric, malic, and glycollic acids have been determined potentiometrically by the iodometric method, using Ba, Zn, or Mg salts as pptg. agents. The liberated I was titrated with Na₂S₂O₃ at 10°, using a Pt electrode coupled with a saturated HgCl electrode.

VII. PhOH, *p*-NO₂C₆H₄NH₂, NHPh₂, and benzoquinone have been determined potentiometrically by titration against standard KClO₃, at 25°, in presence of HCl.

W. R. A.

Rapid determination of esters of volatile fatty acids. L. E. GRANDCHAMP and J. VOLLAIRE-SALVA (Ann. Falsif., 1939, 32, 244—247).—Volatile acidity is determined before and after hydrolysis (NaOH; 20°). The validity of the method is supported by chemical and organoleptic tests, and its forensic application is indicated.

I. A. P.

[Determination of] carotene. V. E. MUNSEY (J. Assoc. Off. Agric. Chem., 1939, 22, 664—673).—Peterson and Hughes' method (cf. *ibid.*, 79) gives consistent results when tested by collaborative analysis. Those by Fraps' and Russell's methods are lower and more variable, but the former may be used when no spectrophotometer is available, using 0.1N-K₂Cr₂O₇ as standard.

E. C. S.

Colorimetric silicomolybdic acid method for determining small quantities of nicotine. G. L. SUTHERLAND, R. P. DAROGA, and A. G. POLLARD (J.S.C.I., 1939, 58, 284—288).—Hofmann's method (B., 1933, 365) is modified. Conditions of pptn. of nicotine silicomolybdate and the subsequent development of the blue colour by aq. glycine-NaHSO₃ requisite for max. colour intensity are prescribed. The method is adapted to determining nicotine (0.2 mg. upward) in steam distillates etc. using the tintometer. Details are given for determinations in soil samples.

A. G. P.

Colour reaction for identification of 8-(diethylaminoisoamyl)amino-6-methoxyquinoline (Plasmoquine, Praequine). A. E. TSCHITSCHIBABIN and C. HOFFMANN (Bull. Sci. Pharmacol., 1939, 41, 231—232).—5 c.c. of 10% HIO₃ are added to 10 c.c. of solution, when a violet coloration develops in presence of ≤ 0.5 p.p.m. of Plasmoquine. The reaction is sp.

R. T.

Reactions of diethylmalonylurea and of certain pyrazolone derivatives. A. PEROTTI (Boll. Chim. farm., 1939, 78, 497—505).—Colour reactions of various compounds and additive products are compared. The product from diethylmalonylurea (I), antipyrine, and 2 mols. of pyrimidone appears to contain no free (I).

E. W. W.

Determination of riboflavin. Fluorometric and biological methods.—See A., 1939, III, 993.

Determination of aneurin by thiochrome reaction with Pulfrich refractometer.—See A., 1939, III, 1070.

Use of amyl alcohol in the Van Slyke method for determining the nitrogen distribution in proteins.—See A., 1939, III, 1113.

Application of micro-methods in analysis of zein.—See A., 1939, III, 1020.